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Structure Determination of Organic Compounds

Tables of Spectral Data

Third Completely Revised and Enlarged English Edition
Corrected first Printing



Springer

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ISBN 3-540-67815-8 Springer-Verlag Berlin Heidelberg New York

CIP-Data applied for

Pretsch, Ernoe: Structure determination of organic compounds : tables of spectral data /
E. Pretsch ; P. Bühlmann ; C. Affolter. - 3., completely rev. and enl. engl. ed..
Berlin ; Heidelberg ; New York ; Barcelona ; Hong Kong ; London ; Milan ; Paris ;
Singapore ; Tokyo : Springer, 2000
ISBN 3-540-67815-8

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Typesetting: Camera-ready by editors
Cover layout: design & production GmbH, Heidelberg
Printed on acid-free paper SPIN: 10896235 52/3020 - 5 4 3 2 1 0 -

Preface

While modern techniques of nuclear magnetic resonance and mass spectrometry changed the ways of data acquisition and greatly extended the capabilities of these methods, the basic parameters, such as chemical shifts, coupling constants, and fragmentation pathways remain the same. This explains the ongoing success of the earlier editions of this book. However, since the amount of available data has considerably increased over the years, we decided to prepare an entirely new manuscript. It follows the same basic concepts, i.e., it provides a representative, albeit limited set of reference data for the interpretation of ^{13}C NMR, ^1H NMR, IR, mass, and UV/Vis spectra. On the other hand, the book has undergone a number of changes. The amount of reference data has been doubled at least (especially for MS and IR) and the order and selection of data for the various spectroscopic methods is now arranged strictly in the same way. In addition, the enclosed compact disc contains programs for estimating NMR chemical shifts and generating isomers based on structural information.

Unfortunately, our teachers and colleagues, Prof. Wilhelm Simon and Prof. Thomas Clerc are no longer among us, and Prof. Joseph Seibl has retired years ago. Their contributions to developing the concept and the earlier editions of this work cannot be overemphasized. We also thank numerous colleagues who helped us in many different ways to complete the manuscript. We are particularly indebted to Dr. Dorothee Wegmann for her expertise with which she eliminated many errors and inconsistencies of the first versions. Special thanks are due to Dr. Rich Knochenmuss (ETH Zürich) for the MALDI mass spectra of matrix materials, Dr. Kikuko Hayamizu for her help with the Spectral Database System of the National Institute of Materials and Chemical Research, Tsukuba, Ibaraki (Japan), Prof. Bernhard Jaun and Dr. Martin Badertscher (ETH Zürich) for critically reading parts of the manuscript. Dr. Martin Badertscher is also thanked for the tutorial of the structure generator, Assemble 2.0, and Upstream Solutions (Hergiswil, Switzerland) for providing free versions of the computer programs on the enclosed compact disk.

In spite of great efforts and many checks to eliminate errors, it is likely that some errors or inconsistencies remain. We would like to encourage our readers to contact us with comments and suggestions or any kind of problems when using the book or the enclosed programs under one of the following addresses: Prof. Ernő Pretsch, Laboratory of Organic Chemistry, CH-8092 Zürich, Switzerland, e-mail: pretsch@org.chem.ethz.ch, or Prof. Philippe Bühlmann, Department of Chemistry, University of Minnesota, 207 Pleasant St., SE, Minneapolis, MN 55455, USA, e-mail: buhlmann@chem.umn.edu.

Zürich and Tokyo, August 2000

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1 Introduction

1.1 Scope and Organization

The present data collection is intended to serve as an aid in the interpretation of molecular spectra for the elucidation and confirmation of the structure of organic compounds. It consists of reference data, spectra, and empirical correlations from ^{13}C and ^1H nuclear magnetic resonance (NMR), infrared (IR), mass, and ultraviolet–visible (UV/vis) spectroscopy. It is to be viewed as a supplement to textbooks and specific reference works dealing with these spectroscopic techniques. The use of this book to interpret spectra only requires the knowledge of basic principles of the techniques, but its content is structured in a way that it will serve as a reference book also to specialists.

Chapters 2 and 3 contain Summary Tables and Combined Tables of the most relevant spectral characteristics of structural elements. While Chapter 2 is organized according to the different spectroscopic techniques, Chapter 3 provides for each class of structural elements spectroscopic information obtained with various techniques. These two chapters should assist users that are less familiar with spectra interpretation to identify the classes of structural elements present in samples of their interest. The following four chapters cover data from ^{13}C NMR, ^1H NMR, IR, and mass spectroscopy, and are ordered exactly in the same manner by compound types. These cover the various skeletons (alkyl, alkenyl, alkynyl, alicyclic, aromatic, and heteroaromatic), the most important substituents (halogen, single-bonded oxygen, nitrogen, sulfur, and carbonyl), and some specific compound classes (miscellaneous compounds and natural products). Finally, a spectra collection of common solvents, auxiliary compounds (such as matrix materials and references) and commonly found impurities is provided for each method. Not only the strictly analogous order of the data but also the optical marks on the edge of the pages help fast cross-referencing between the various spectroscopic techniques. Although currently, UV/vis spectroscopy is only marginally relevant to structure elucidation, its importance might increase by the advent of high throughput analyses. Also, the reference data presented in Chapter 8 are useful in connection with optical sensors and the widely applied UV/vis detectors in chromatography and electrophoresis.

Since a large part of the tabulated data either comes from our own measurements or is based on a large body of literature data, comprehensive references to published sources are generally not included. Whenever possible, the

data refers to conventional modes and conditions of measurement. For example, unless the solvent is indicated, the NMR chemical shifts were determined usually with deuteriochloroform or carbon tetrachloride as solvent. Likewise, the IR spectra were measured using solvents of low polarity, such as chloroform or carbon disulfide. Mass spectral data were recorded with electron impact ionization at 70 eV.

While retaining the basic structure of the previous editions, numerous new entries have been added. Altogether, the amount of data has been more than doubled. The section on mass spectrometry (MS) is entirely new and contains a unique collection of fragmentation rules for the various compound classes. As a new feature, prototype IR spectra for each class of compounds schematically show the analytically relevant absorption bands. The Combination Tables of the earlier editions have been extended and arranged in two chapters, the first organized according to band positions and the second according to compound classes.

The enclosed compact disc contains programs for estimating ^{13}C and ^1H chemical shifts of organic compounds containing up to 15 non-hydrogen atoms. Both programs are available for Windows and Macintosh systems and require a Java environment for the graphical structure input. Technical details about the requirements and installation procedures are given in the corresponding ReadMe files. Extensive help files are available as part of the programs. In addition, the structure generator Assemble 2.0 (also limited to 15 non-hydrogen atoms) is available for Windows systems. Based on the molecular formula and available structural information, it is capable of generating all possible structural isomers. An extensive hypertext based tutorial describes its main features. It is especially recommended as a quality control tool to check if alternative solutions that also agree with the experimental data have gone unnoticed.

1.2 Abbreviations and Symbols

al	aliphatic
alk	alkyl
alken	alkenyl
ar	aromatic
as	asymmetric
ax	axial
comb	combination frequency
d	doublet
δ	IR: deformation vibration NMR: chemical shift
DMSO	dimethyl sulfoxide
eq	equatorial
ϵ	molar absorptivity
Frag	fragment
γ	skeletal vibration
gem	geminal
hal	halogen
ip	in plane vibration
J	coupling constant
$M^{+\cdot}$	molecular radical ion
m/z	mass to charge ratio
v	frequency
oop	out of plane vibration
sh	shoulder
st	stretching vibration
sy	symmetric
TMS	tetramethylsilane
vic	vicinal

2 Summary Tables

2.1 General Tables

2.1.1 Calculation of the Number of Double Bond Equivalents from the Molecular Formula

General Equation:

$$\text{double bond equivalents} = \frac{2 + \sum_i n_i (v_i - 2)}{2}$$

n_i : number of atoms of element i in molecular formula
 v_i : formal valence of element i

Short Cut:

For compounds containing only C, H, O, N, S, and halogens, the following steps permit a quick and simple calculation of the number of double bond equivalents:

1. O and divalent S are deleted from the molecular formula
2. Halogens are replaced by hydrogen
3. Trivalent N is replaced by CH
4. The resulting hydrocarbon, C_nH_x , is compared with the saturated hydrocarbon, C_nH_{2n+2} . Each double bond equivalent reduces the number of hydrogen atoms by 2:

$$\text{double bond equivalents} = \frac{2n + 2 - x}{2}$$

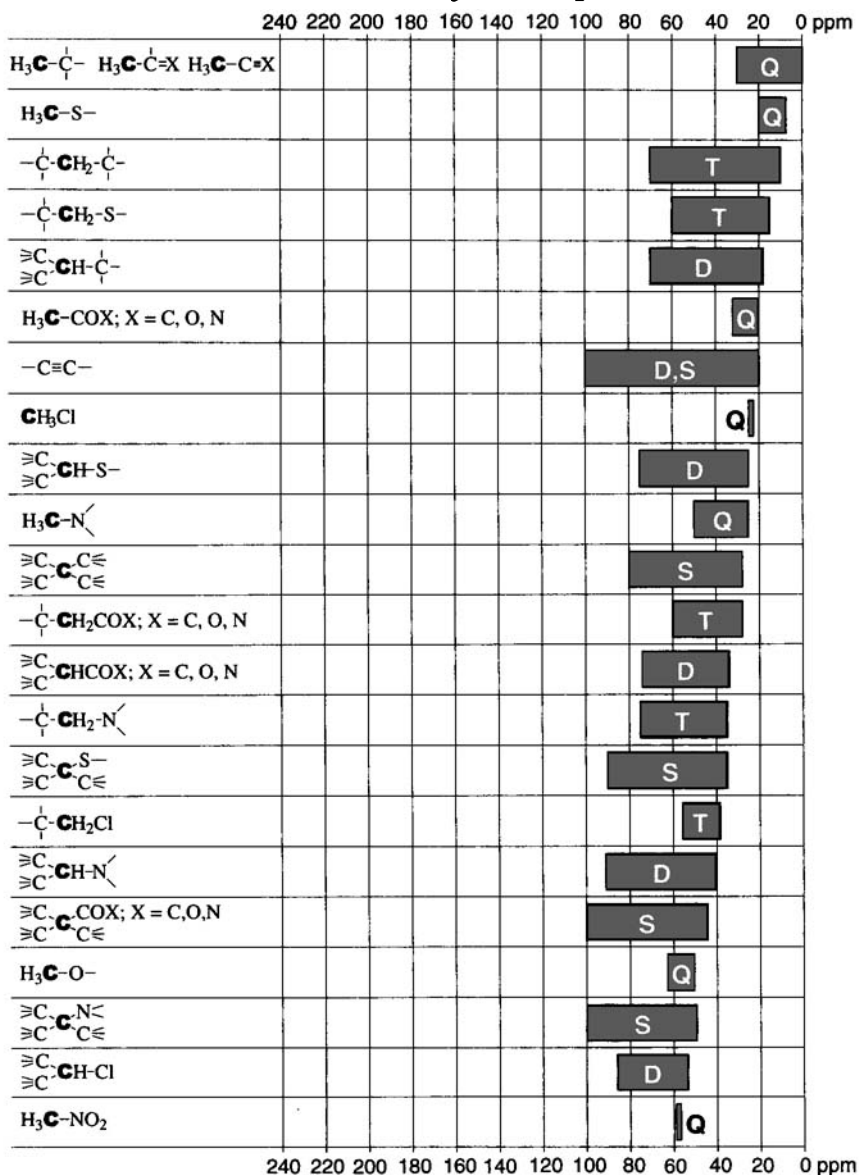
2.1.2
Properties of Selected Nuclei

Isotope	Natural abundance [%]	Spin quantum number, I	Frequency [MHz] at 2.35 Tesla	Relative sensitivity of nucleus	Relative sensitivity at natural abundance	Electric quadrupole moment [$e \times 10^{-24} \text{ cm}^2$]
^1H	99.985	1/2	100.0	1	1	
^2H	0.015	1	15.4	9.6×10^{-3}	1.5×10^{-6}	2.8×10^{-3}
^3H	0.000	1/2	106.7	1.2	0	
^{10}B	19.58	3	10.7	2.0×10^{-2}	3.9×10^{-3}	7.4×10^{-2}
^{11}B	80.42	3/2	32.1	1.6×10^{-1}	1.3×10^{-1}	3.6×10^{-2}
^{13}C	1.108	1/2	25.1	1.6×10^{-2}	1.8×10^{-4}	
^{14}N	99.635	1	7.3	1.0×10^{-3}	1.0×10^{-3}	1.9×10^{-2}
^{15}N	0.365	1/2	10.1	1.0×10^{-3}	3.8×10^{-6}	
^{17}O	0.037	5/2	13.6	2.9×10^{-2}	1.1×10^{-5}	-2.6×10^{-2}
^{19}F	100.000	1/2	94.1	8.3×10^{-1}	8.3×10^{-1}	
^{31}P	100.000	1/2	40.5	6.6×10^{-2}	6.6×10^{-2}	
^{33}S	0.76	3/2	7.6	2.3×10^{-3}	1.7×10^{-5}	-6.4×10^{-2}
^{117}Sn	7.61	1/2	35.6	4.5×10^{-2}	3.4×10^{-3}	
^{119}Sn	8.58	1/2	37.3	5.2×10^{-2}	4.4×10^{-3}	
^{195}Pt	33.8	1/2	21.5	9.9×10^{-3}	3.4×10^{-3}	
^{199}Hg	16.84	1/2	17.8	5.7×10^{-3}	9.5×10^{-4}	
^{207}Pb	22.6	1/2	20.9	9.2×10^{-3}	2.1×10^{-4}	

2.2

^{13}C NMR Spectroscopy

Summary of the Regions of Chemical Shifts, δ , for Carbon Atoms in Various Chemical Environments (δ in ppm relative to TMS. Carbon atoms are specified as follows: Q for CH_3 , T for CH_2 , D for CH , and S for C).



^{13}C Chemical Shifts for Carbonyl Groups (δ in ppm relative to TMS)

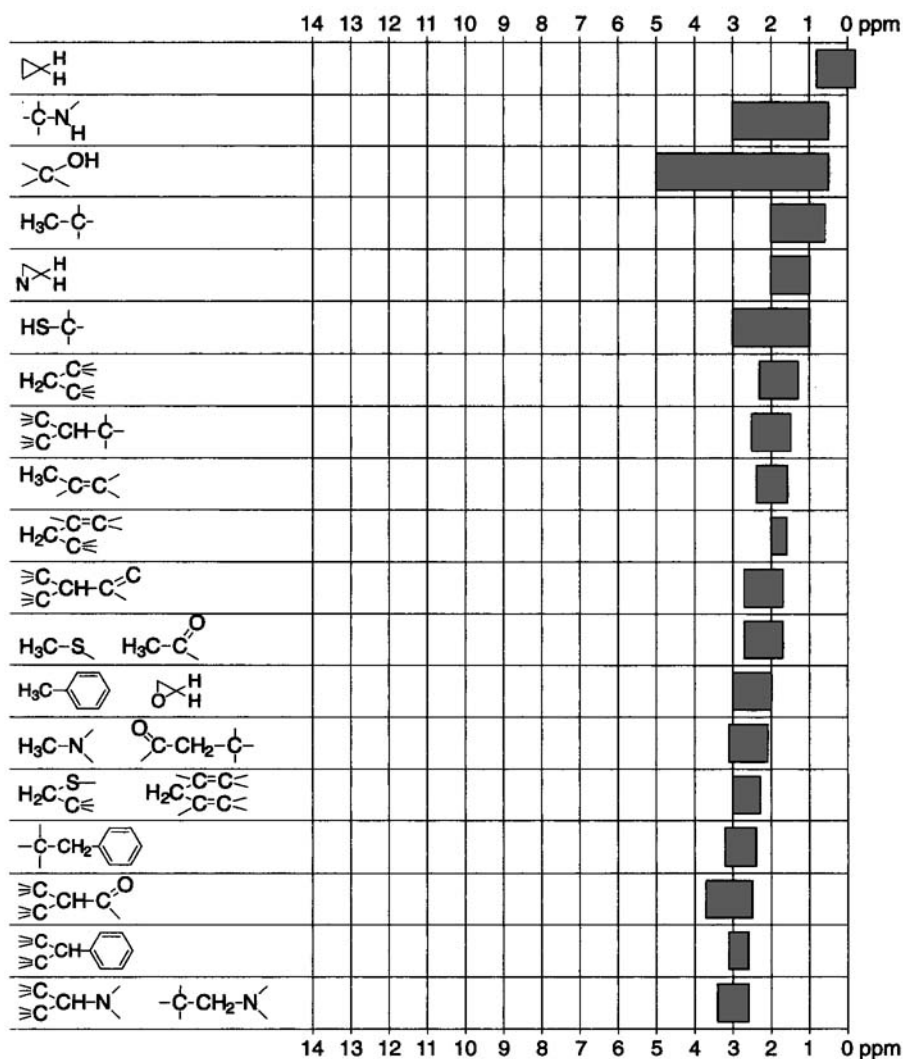
R	R-CHO	R-COCH ₃	R-COOH	R-COO ⁻
-H	197.0	200.5	166.3	171.3
-CH ₃	200.5	206.7	176.9	182.6
-CH ₂ CH ₃	202.7	207.6	180.4	185.1
-CH(CH ₃) ₂	204.6	211.8	184.1	
-C(CH ₃) ₃	205.6	213.5	185.9	188.6
- <i>n</i> -C ₈ H ₁₇	202.6	207.9	180.7	183.1
-CH ₂ Cl	193.3	200.1	173.7	175.9
-CHCl ₂		193.6	170.4	171.8
-CCl ₃	176.9	186.3	167.1	167.6
-cyclohexyl	204.7	209.4	182.1	185.4
-CH=CH ₂	194.4	197.5	171.7	174.5
-C≡CH	176.8		156.5	
-phenyl	192.0	196.9	172.6	177.6

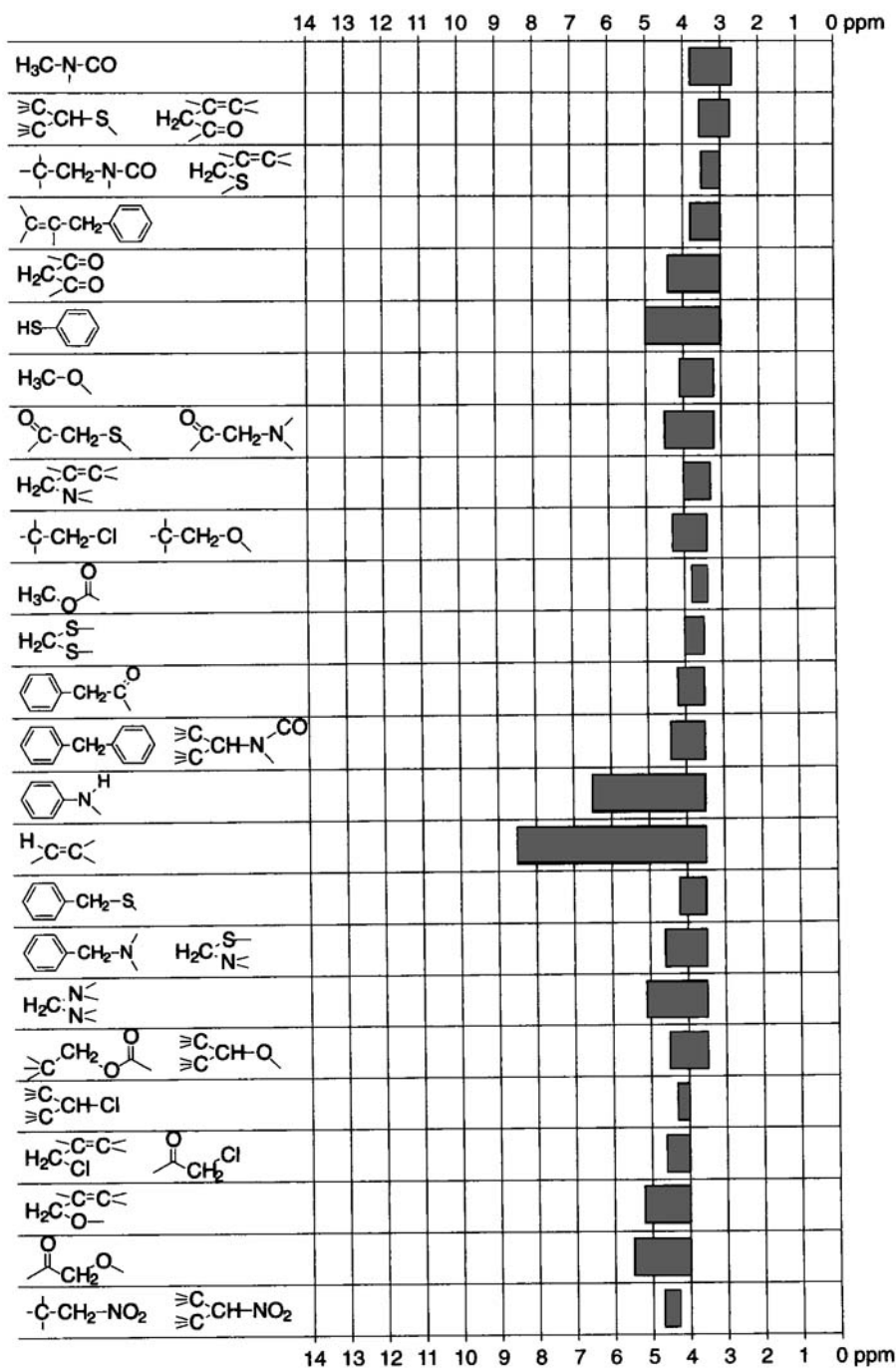
R	R-COOCH ₃	R-CONH ₂	R-COOCO-R	R-COCl
-H	161.6	167.6	158.5	
-CH ₃	171.3	173.4	167.4	170.4
-CH ₂ CH ₃	173.3	177.2	170.3	174.7
-CH(CH ₃) ₂	177.4		172.8	178.0
-C(CH ₃) ₃	178.8	180.9	173.9	180.3
- <i>n</i> -C ₈ H ₁₇	174.4	176.3	169.4	173.8
-CH ₂ Cl	167.8	168.3	162.1	167.7
-CHCl ₂	165.1		157.6	165.5
-CCl ₃	162.5		154.1	
-cyclohexyl	175.3	177.3		176.3
-CH=CH ₂	166.5	168.3		165.6
-C≡CH	153.4			
-phenyl	166.8	169.7	162.8	168.0

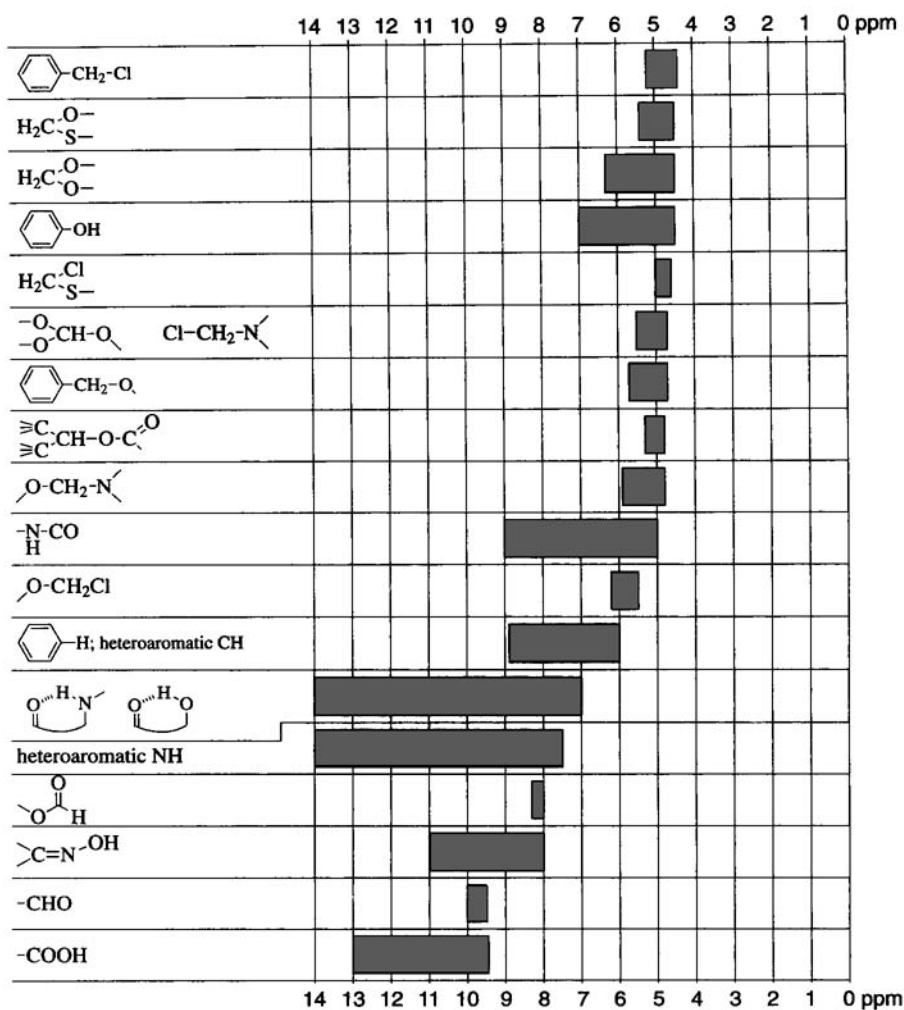
2.3

 ^1H NMR Spectroscopy

Summary of the Regions of Chemical Shifts for Hydrogen Atoms in Various Chemical Environments (δ in ppm relative to TMS)

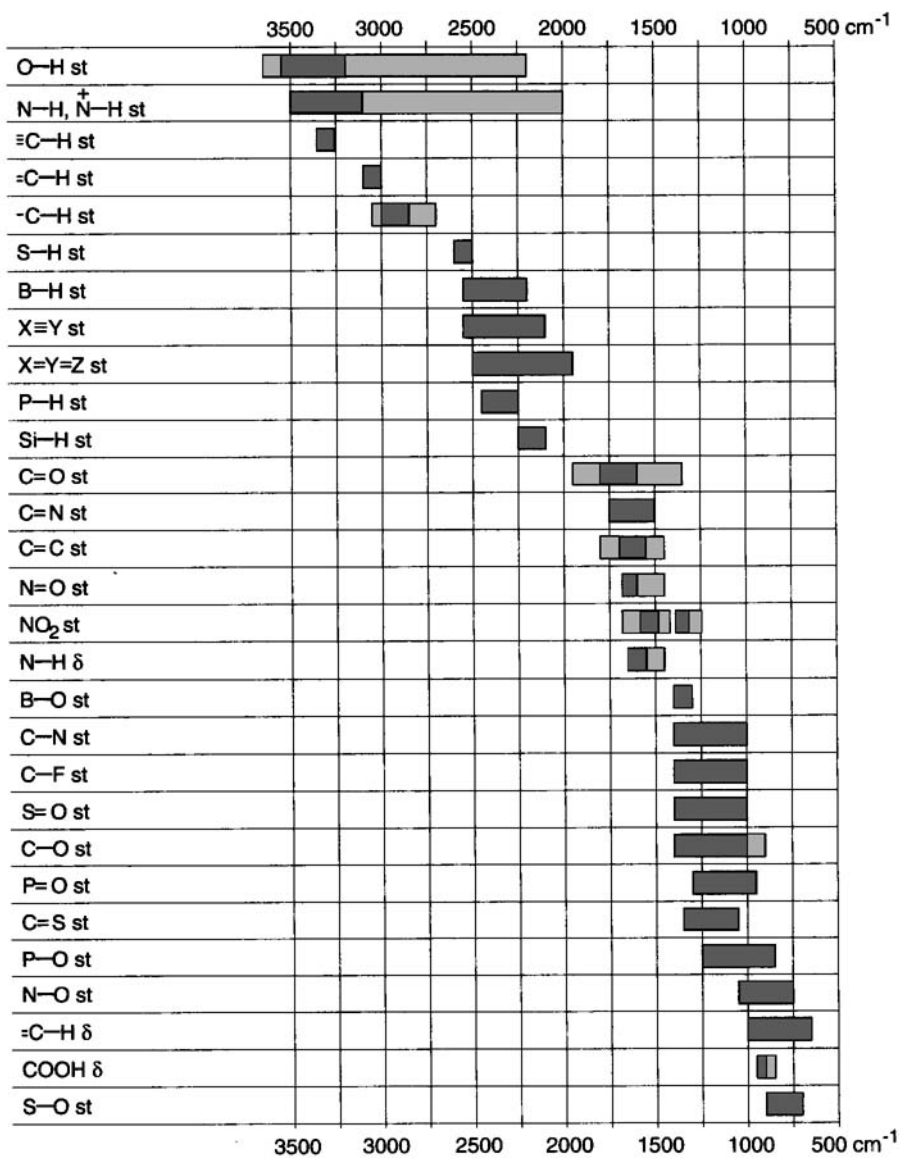




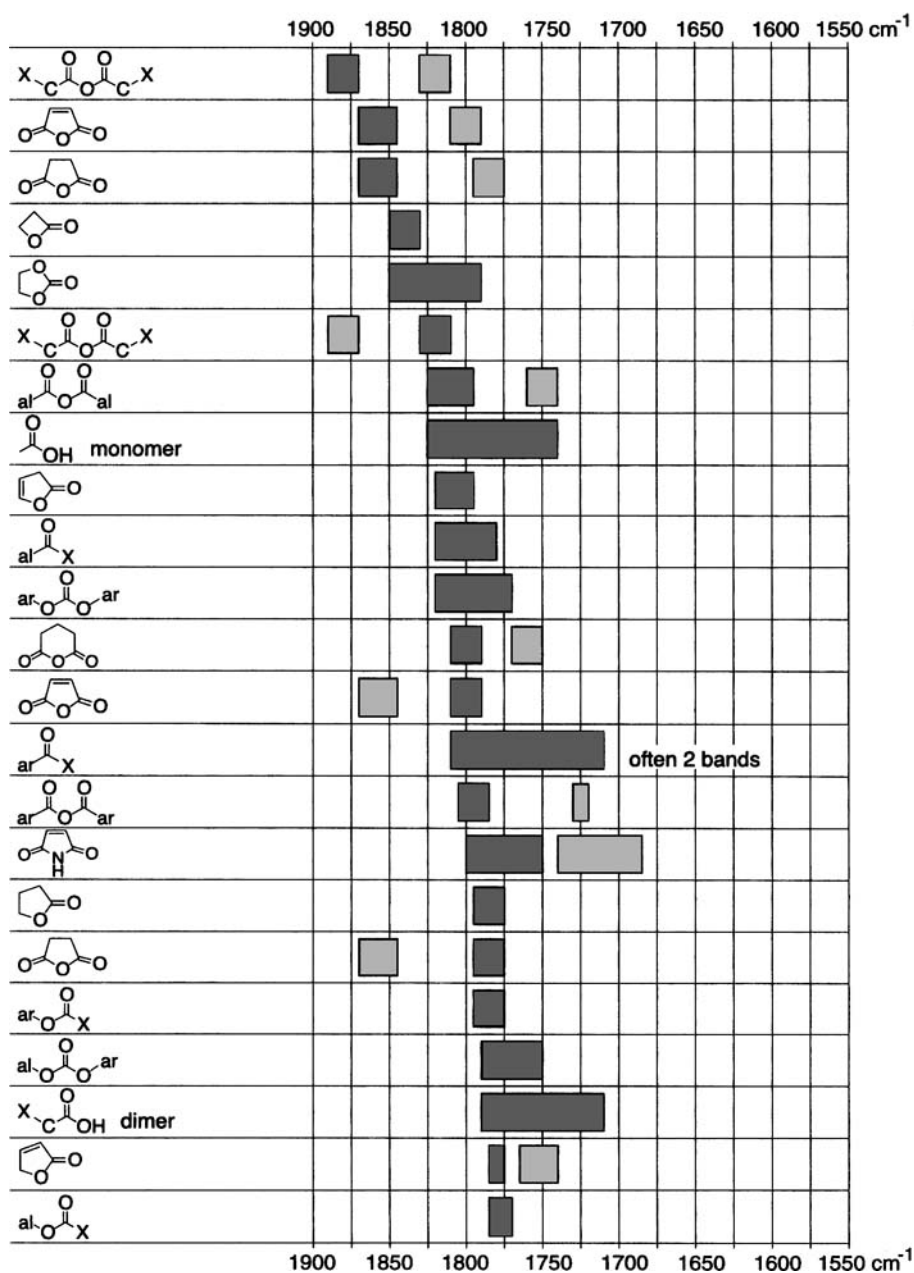


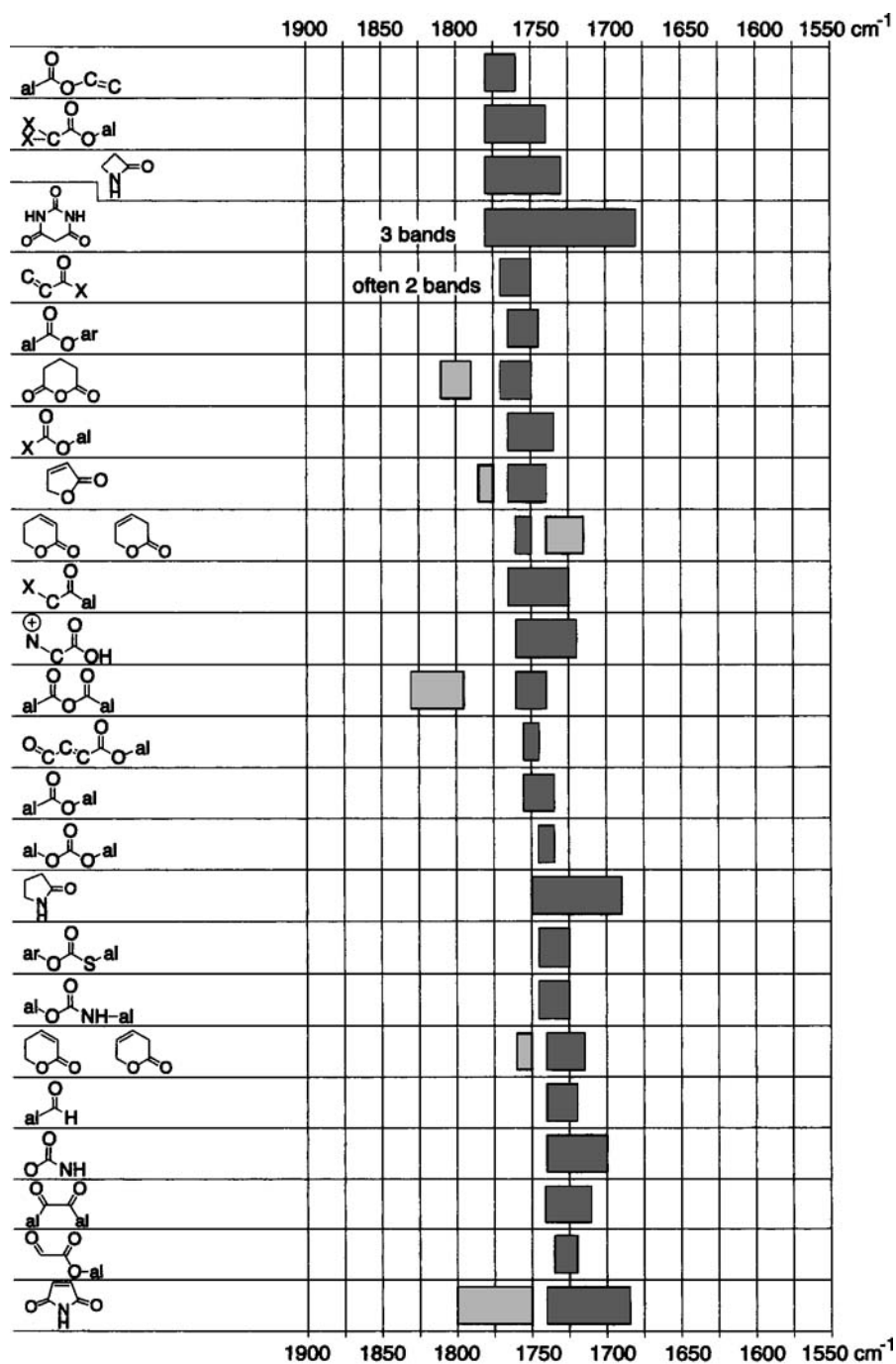
2.4 IR Spectroscopy

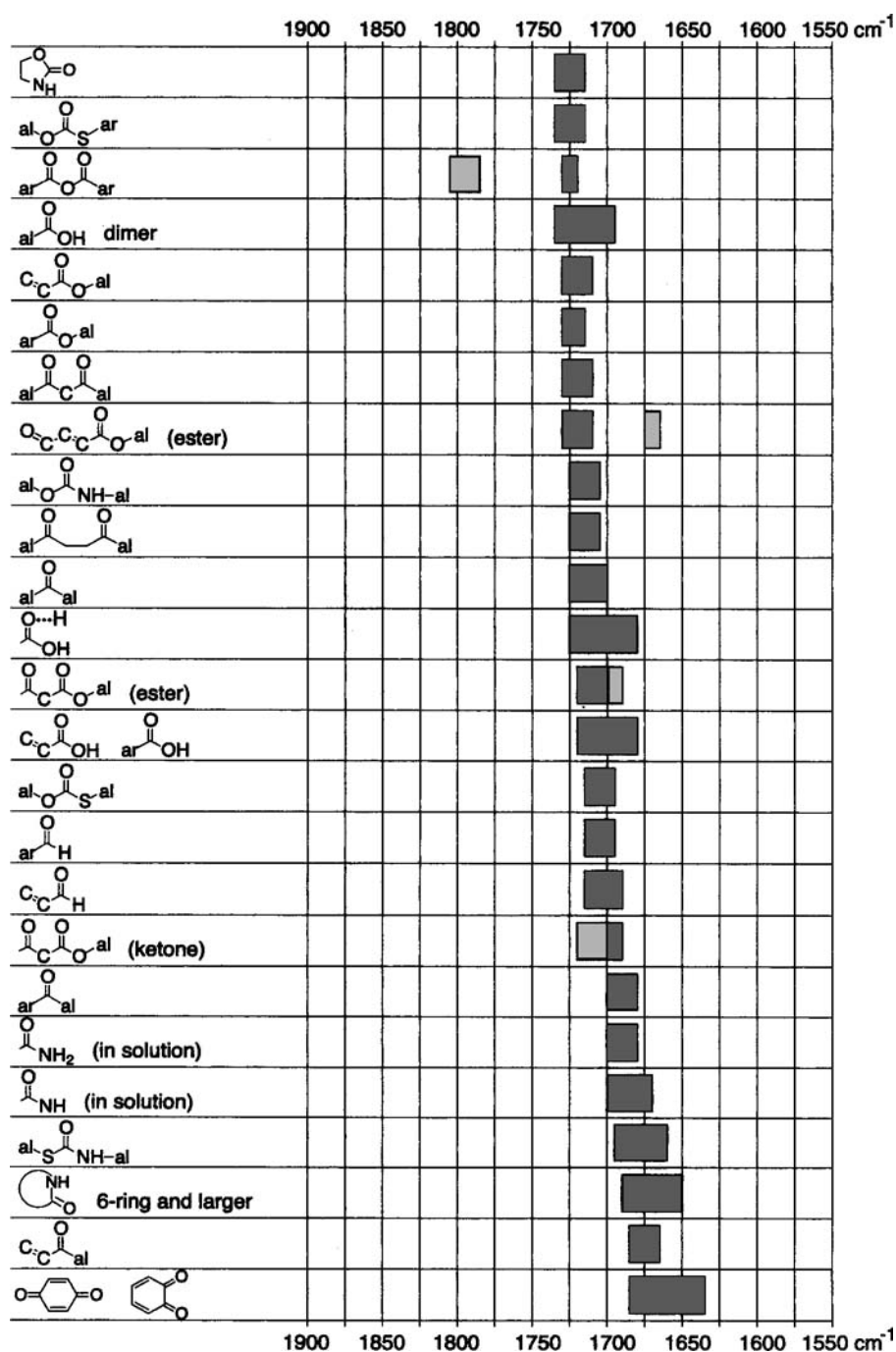
Summary of the Most Important IR Absorption Bands

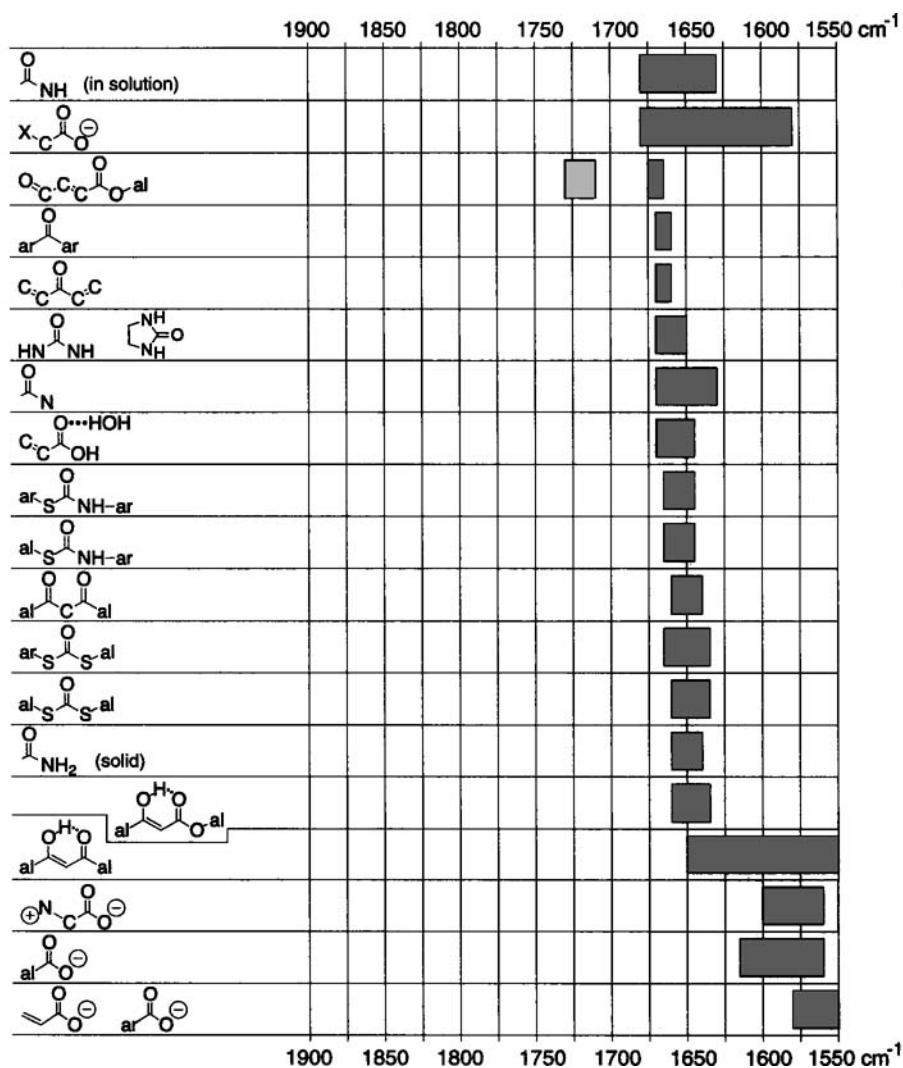


Summary of IR Absorption Bands of Carbonyl Groups (in cm^{-1})









2.5 Mass Spectrometry

2.5.1 Average Masses of Naturally Occurring Elements with Exact Masses and Representative Relative Abundances of Isotopes [1-3]

Element	Mass	Abundance	Element	Mass	Abundance
Isotope			Isotope		
H	1.00795 ^a		Ne	20.1798 ^a	
¹ H	1.007825	100 ^b	²⁰ Ne	19.992402	100 ^b
² H	2.014101	0.0115	²¹ Ne	20.993847	0.30
	(in water)		²² Ne	21.991386	10.22
				(in air)	
He	4.002602 ^a		Na	22.989769	
³ He	3.016029	0.000137	²³ Na	22.989769	100
⁴ He	4.002603	100			
	(in air)		Mg	24.3051	
Li	6.941 ^a		²⁴ Mg	23.985042	100
⁶ Li	6.015122	8.21 ^c	²⁵ Mg	24.985837	12.66
⁷ Li	7.016004	100	²⁶ Mg	25.982593	13.94
Be	9.012182		Al	26.981538	
⁹ Be	9.012182	100	²⁷ Al	26.981538	100
B	10.812 ^a		Si	28.0855 ^a	
¹⁰ B	10.012937	24.8 ^b	²⁸ Si	27.976927	100
¹¹ B	11.009306	100	²⁹ Si	28.976495	5.0778
			³⁰ Si	29.973770	3.3473
C	12.0108 ^a		P	30.973762	
¹² C	12.000000	100	³¹ P	30.973762	100
¹³ C	13.003355	1.08			
N	14.00675 ^a		S	32.067 ^a	
¹⁴ N	14.003070	100	³² S	31.972071	100
¹⁵ N	15.000109	0.369	³³ S	32.971459	0.80
			³⁴ S	33.967867	4.52
O	15.9994 ^a		³⁶ S	35.967081	0.02
¹⁶ O	15.994915	100	Cl	35.4528	
¹⁷ O	16.999132	0.038	³⁵ Cl	34.968853	100 ^b
¹⁸ O	17.999116	0.205	³⁷ Cl	36.965903	31.96
F	18.998403				
¹⁹ F	18.998403	100			

Element Isotope	Mass	Abundance	Element Isotope	Mass	Abundance
Ar	39.948 ^a		⁵⁷ Fe	56.935399	2.309
³⁶ Ar	35.967546	0.3379	⁵⁸ Fe	57.933280	0.307
³⁸ Ar	37.962776	0.0635	Co	58.933200 ^a	
⁴⁰ Ar	39.962383	100 (in air)	⁵⁹ Co	58.933200	100
K	39.0983		Ni	58.6934	
³⁹ K	38.963706	100	⁵⁸ Ni	57.935348	100
⁴⁰ K	39.963999	0.0125	⁶⁰ Ni	59.930791	38.5198
⁴¹ K	40.961826	7.2167	⁶¹ Ni	60.931060	1.6744
Ca	40.078		⁶² Ni	61.928349	5.3388
⁴⁰ Ca	39.962591	100	⁶⁴ Ni	63.927970	1.3596
⁴² Ca	41.958618	0.667	Cu	63.546	
⁴³ Ca	42.958769	0.139	⁶³ Cu	62.929601	100
⁴⁴ Ca	43.955481	2.152	⁶⁵ Cu	64.927794	44.57
⁴⁶ Ca	45.953693	0.004	Zn	65.39	
⁴⁸ Ca	47.952534	0.193	⁶⁴ Zn	63.929147	100
Sc	44.955910		⁶⁶ Zn	65.926037	57.37
⁴⁵ Sc	44.955910	100	⁶⁷ Zn	66.927131	8.43
Ti	47.867		⁶⁸ Zn	67.924848	38.56
⁴⁶ Ti	45.952629	11.19	⁷⁰ Zn	69.925325	1.27
⁴⁷ Ti	46.951764	10.09	Ga	69.723	
⁴⁸ Ti	47.947947	100	⁶⁹ Ga	68.925581	100 ^b
⁴⁹ Ti	48.947871	7.34	⁷¹ Ga	70.924705	66.367
⁵⁰ Ti	49.944792	7.03	Ge	72.61	
V	50.9415		⁷⁰ Ge	69.924250	56.44
⁵⁰ V	49.947163	0.250	⁷² Ge	71.922076	75.91
⁵¹ V	50.943964	100	⁷³ Ge	72.923459	21.31
Cr	51.9962		⁷⁴ Ge	73.921178	100
⁵⁰ Cr	49.946050	5.187	⁷⁶ Ge	75.921403	20.98
⁵² Cr	51.940512	100	As	74.921596	
⁵³ Cr	52.940654	11.339	⁷⁵ As	74.921596	100
⁵⁴ Cr	53.938885	2.823	Se	78.96	
Mn	54.938050		⁷⁴ Se	73.922477	1.79
⁵⁵ Mn	54.938050	100	⁷⁶ Se	75.919214	18.89
Fe	55.845		⁷⁷ Se	76.919915	15.38
⁵⁴ Fe	53.939615	6.370	⁷⁸ Se	77.917310	47.91
⁵⁶ Fe	55.934942	100	⁸⁰ Se	79.916522	100
			⁸² Se	81.916700	17.60

Element Isotope	Mass	Abundance
Br	79.904	
⁷⁹ Br	78.918338	100
⁸¹ Br	80.916291	97.28
Kr	83.80	
⁷⁸ Kr	77.920387	0.61 ^b
⁸⁰ Kr	79.916378	4.00
⁸² Kr	81.913485	20.32
⁸³ Kr	82.914136	20.16
⁸⁴ Kr	83.911507	100
⁸⁶ Kr	85.910610	30.35
	(in air)	
Rb	85.4678	
⁸⁵ Rb	84.911789	100
⁸⁷ Rb	86.909183	38.56
Sr	87.62 ^a	
⁸⁴ Sr	83.913425	0.68
⁸⁶ Sr	85.909262	11.94
⁸⁷ Sr	86.908879	8.48
⁸⁸ Sr	87.905614	100
Y	88.905848	
⁸⁹ Y	88.905848	100
Zr	91.224	
⁹⁰ Zr	89.904704	100
⁹¹ Zr	90.905645	21.81
⁹² Zr	91.905040	33.33
⁹⁴ Zr	93.906316	33.78
⁹⁶ Zr	95.908276	5.44
Nb	92.906378	
⁹³ Nb	92.906378	100
Mo	95.94	
⁹² Mo	91.906810	61.50
⁹⁴ Mo	93.905088	38.33
⁹⁵ Mo	94.905841	65.98
⁹⁶ Mo	95.904679	69.13
⁹⁷ Mo	96.906021	39.58
⁹⁸ Mo	97.905408	100
¹⁰⁰ Mo	99.907478	39.91

Element Isotope	Mass	Abundance
Ru	101.07	
⁹⁶ Ru	95.907599	17.56
⁹⁸ Ru	97.905288	5.93
⁹⁹ Ru	98.905939	40.44
¹⁰⁰ Ru	99.904229	39.94
¹⁰¹ Ru	100.905582	54.07
¹⁰² Ru	101.904350	100
¹⁰⁴ Ru	103.905430	59.02
Rh	102.905504	
¹⁰³ Rh	102.905504	100
Pd	106.42	
¹⁰² Pd	101.905608	3.73
¹⁰⁴ Pd	103.904036	40.76
¹⁰⁵ Pd	104.905084	81.71
¹⁰⁶ Pd	105.903484	100
¹⁰⁸ Pd	107.903894	96.82
¹¹⁰ Pd	109.905151	42.88
Ag	107.8682	
¹⁰⁷ Ag	106.905094	100
¹⁰⁹ Ag	108.904756	92.90
Cd	112.412	
¹⁰⁶ Cd	105.906459	4.35
¹⁰⁸ Cd	107.904184	3.10
¹¹⁰ Cd	109.903006	43.47
¹¹¹ Cd	110.904182	44.55
¹¹² Cd	111.902757	83.99
¹¹³ Cd	112.904401	42.53
¹¹⁴ Cd	113.903358	100
¹¹⁶ Cd	115.904755	26.07
In	114.818	
¹¹³ In	112.904061	4.48
¹¹⁵ In	114.903879	100
Sn	118.711	
¹¹² Sn	111.904822	2.98
¹¹⁴ Sn	113.902782	2.03
¹¹⁵ Sn	114.903346	1.04
¹¹⁶ Sn	115.901744	44.63
¹¹⁷ Sn	116.902954	23.57
¹¹⁸ Sn	117.901606	74.34

(contd.)

Element Isotope	Mass	Abundance	Element Isotope	Mass	Abundance
¹¹⁹ Sn	118.903309	26.37	La	138.9055	
¹²⁰ Sn	119.902197	100	¹³⁸ La	137.907107	0.090
¹²¹ Sn	121.903440	14.21	¹³⁹ La	138.906348	100
¹²⁴ Sn	123.905275	17.77	Ce	140.116	
Sb	121.760		¹³⁶ Ce	135.907145	0.209
¹²¹ Sb	120.903818	100	¹³⁸ Ce	137.905991	0.284
¹²³ Sb	122.904216	74.79	¹⁴⁰ Ce	139.905434	100
Te	127.60		¹⁴² Ce	141.909240	12.565
¹²⁰ Te	119.904021	0.26	Pr	140.907648	
¹²² Te	121.903047	7.48	¹⁴¹ Pr	140.907648	100
¹²³ Te	122.904273	2.61	Nd	144.24	
¹²⁴ Te	123.902819	13.91	¹⁴² Nd	141.907719	100
¹²⁵ Te	124.904425	20.75	¹⁴³ Nd	142.909810	44.9
¹²⁶ Te	125.903306	55.28	¹⁴⁴ Nd	143.910083	87.5
¹²⁸ Te	127.904461	93.13	¹⁴⁵ Nd	144.912569	30.5
¹³⁰ Te	129.906223	100	¹⁴⁶ Nd	145.913112	63.2
I	126.904468		¹⁴⁸ Nd	147.916889	21.0
¹²⁷ I	126.904468	100	¹⁵⁰ Nd	149.920887	20.6
Xe	131.29		Sm	150.36	
¹²⁴ Xe	123.905896	0.33 ^b	¹⁴⁴ Sm	143.911995	11.48
¹²⁶ Xe	125.904270	0.33	¹⁴⁷ Sm	146.914893	56.04
¹²⁸ Xe	127.903530	7.14	¹⁴⁸ Sm	147.914818	42.02
¹²⁹ Xe	128.904779	98.33	¹⁴⁹ Sm	148.917180	51.66
¹³⁰ Xe	129.903508	15.17	¹⁵⁰ Sm	149.917271	27.59
¹³¹ Xe	130.905082	78.77	¹⁵² Sm	151.919728	100
¹³² Xe	131.904154	100	¹⁵⁴ Sm	153.922205	85.05
¹³⁴ Xe	133.905395	38.82	Eu	151.964	
¹³⁶ Xe	135.907221	32.99	¹⁵¹ Eu	150.919846	91.61
Cs	132.905447		¹⁵³ Eu	152.921226	100
¹³³ Cs	132.905447	100	Gd	157.25	
Ba	137.328		¹⁵² Gd	151.919788	0.81
¹³⁰ Ba	129.906311	0.148	¹⁵⁴ Gd	153.920862	8.78
¹³² Ba	131.905056	0.141	¹⁵⁵ Gd	154.922619	59.58
¹³⁴ Ba	133.904503	3.371	¹⁵⁶ Gd	155.922120	82.41
¹³⁵ Ba	134.905683	9.194	¹⁵⁷ Gd	156.923957	63.00
¹³⁶ Ba	135.904570	10.954	¹⁵⁸ Gd	157.924101	100
¹³⁷ Ba	136.905821	15.666	¹⁶⁰ Gd	159.927051	88.00
¹³⁸ Ba	137.905241	100	Tb	158.925343	
			¹⁵⁹ Tb	158.925343	100

Element Isotope	Mass	Abundance
Dy	162.50	
¹⁵⁶ Dy	155.924279	0.21
¹⁵⁸ Dy	157.924405	0.35
¹⁶⁰ Dy	159.925194	8.30
¹⁶¹ Dy	160.926930	67.10
¹⁶² Dy	161.926795	90.53
¹⁶³ Dy	162.928728	88.36
¹⁶⁴ Dy	163.929171	100
Ho	164.930319	
¹⁶⁵ Ho	164.930319	100
Er	167.26	
¹⁶² Er	161.928775	0.42
¹⁶⁴ Er	163.929197	4.79
¹⁶⁶ Er	165.930290	100
¹⁶⁷ Er	166.932045	68.22
¹⁶⁸ Er	167.932368	79.69
¹⁷⁰ Er	169.935460	44.42
Tm	168.934211	
¹⁶⁹ Tm	168.934211	100
Yb	173.04	
¹⁶⁸ Yb	167.933894	0.41
¹⁷⁰ Yb	169.934759	9.55
¹⁷¹ Yb	170.936322	44.86
¹⁷² Yb	171.936378	68.58
¹⁷³ Yb	172.938207	50.68
¹⁷⁴ Yb	173.938858	100
¹⁷⁶ Yb	175.942568	40.09
Lu	174.967	
¹⁷⁵ Lu	174.940768	100
¹⁷⁶ Lu	175.942682	2.66
Hf	178.49	
¹⁷⁴ Hf	173.940040	0.46
¹⁷⁶ Hf	175.941402	14.99
¹⁷⁷ Hf	176.943220	53.02
¹⁷⁸ Hf	177.943698	77.77
¹⁷⁹ Hf	178.944815	38.83
¹⁸⁰ Hf	179.946549	100
Ta	180.9479	
¹⁸⁰ Ta	179.947466	0.012

Element Isotope	Mass	Abundance
¹⁸¹ Ta	180.947996	100
W	183.84	
¹⁸⁰ W	179.946707	0.40
¹⁸² W	181.948206	86.49
¹⁸³ W	182.950224	46.70
¹⁸⁴ W	183.950933	100
¹⁸⁶ W	185.954362	93.79
Re	186.207	
¹⁸⁵ Re	184.952956	59.74
¹⁸⁷ Re	186.955751	100
Os	190.23	
¹⁸⁴ Os	183.952491	0.05
¹⁸⁶ Os	185.953838	3.90
¹⁸⁷ Os	186.955748	4.81
¹⁸⁸ Os	187.955836	32.47
¹⁸⁹ Os	188.958145	39.60
¹⁹⁰ Os	189.958445	64.39
¹⁹² Os	191.961479	100
Ir	192.217	
¹⁹¹ Ir	190.960591	59.49
¹⁹³ Ir	192.962924	100
Pt	195.078	
¹⁹⁰ Pt	189.959931	0.041
¹⁹² Pt	191.961035	2.311
¹⁹⁴ Pt	193.962664	97.443
¹⁹⁵ Pt	194.964774	100
¹⁹⁶ Pt	195.964935	74.610
¹⁹⁸ Pt	197.967876	21.172
Au	196.966552	
¹⁹⁷ Au	196.966552	100
Hg	200.59	
¹⁹⁶ Hg	195.965815	0.50
¹⁹⁸ Hg	197.966752	33.39
¹⁹⁹ Hg	198.968262	56.50
²⁰⁰ Hg	199.968309	77.36
²⁰¹ Hg	200.970285	44.14
²⁰² Hg	201.970626	100
²⁰⁴ Hg	203.973476	23.00

Element			Element		
Isotope	Mass	Abundance	Isotope	Mass	Abundance
Tl	204.3833		Bi	208.980383	
²⁰³ Tl	202.972329	41.892	²⁰⁹ Bi	208.980383	100
²⁰⁵ Tl	204.974412	100			
Pb	207.2 ^a		Th	232.038050	
²⁰⁴ Pb	203.973029	2.7	²³² Th	232.038050	100
²⁰⁶ Pb	205.974449	46.0			
²⁰⁷ Pb	206.975881	42.2	U	238.0289	
²⁰⁸ Pb	207.976636	100	²³⁴ U	234.040946	0.0055 ^d
			²³⁵ U	235.043923	0.73
			²³⁸ U	238.050783	100

- ^a Natural variations in the isotopic composition of terrestrial material does not allow to give a more precise value.
- ^b Commercially available materials may have substantially different isotopic compositions if they were subjected to undisclosed or inadvertent isotopic fractionation.
- ^c Materials depleted in ⁶Li are commercial sources of laboratory shelf reagents and are known to have ⁶Li abundances in the range of 2.0007-7.672 atom percent, with natural materials at the higher end of this range. Average atomic masses vary between 6.939 and 6.996; if a more accurate value is required, it must be determined for the specific material.
- ^d Materials depleted in ²³⁵U are commercial sources of laboratory shelf reagents.

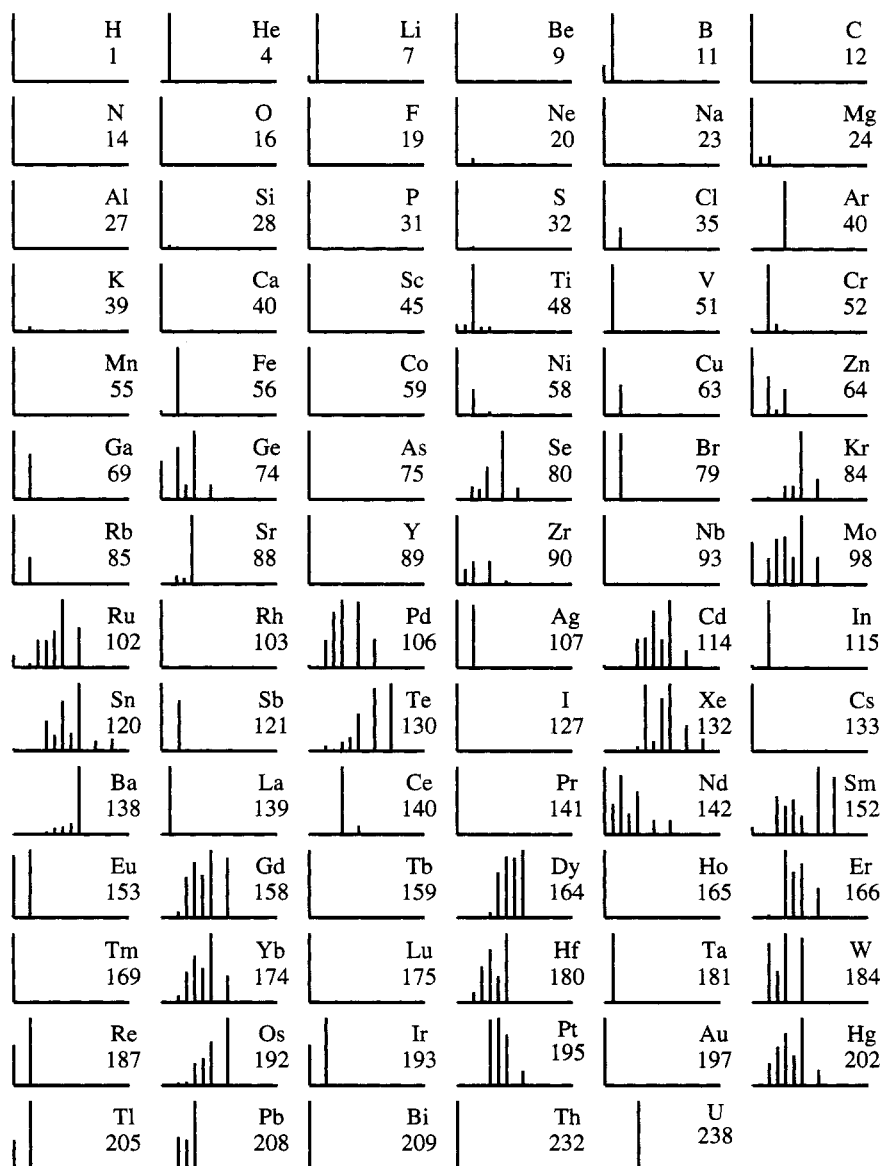
2.5.2

Ranges of Natural Isotope Abundances of Selected Elements
[3]

Element Isotope	Range (atom %)	Element Isotope	Range (atom %)	Element Isotope	Range (atom %)
H		Si		Ce	
¹ H	99.9816–99.9975	²⁸ Si	92.21–92.25	¹³⁶ Ce	0.186–0.185
² H	0.0184–0.0025	²⁹ Si	4.69–4.67	¹³⁸ Ce	0.254–0.251
		³⁰ Si	3.10–3.08	¹⁴⁰ Ce	88.449–88.446
He				¹⁴² Ce	11.114–11.114
³ He	4.6x10 ⁻⁸ –0.0041	S			
⁴ He	100–99.9959	³² S	94.537–95.261	Nd	
		³³ S	0.787–0.731	¹⁴² Nd	27.30–26.80
Li		³⁴ S	4.655–3.993	¹⁴³ Nd	12.32–12.12
⁶ Li	7.21–7.71	³⁶ S	0.021–0.015	¹⁴⁴ Nd	23.97–23.795
⁷ Li	92.79–92.29			¹⁴⁵ Nd	8.35–8.23
		Cl		¹⁴⁶ Nd	17.35–17.06
B		³⁵ Cl	75.64–75.86	¹⁴⁸ Nd	5.78–5.66
¹⁰ B	18.927–20.337	³⁷ Cl	24.36–24.14	¹⁵⁰ Nd	5.69–5.53
¹¹ B	81.073– 79.663				
C		Ca		Hf	
¹² C	98.85–99.02	⁴⁰ Ca	96.982–96.880	¹⁷⁴ Hf	0.1621–0.1619
¹³ C	1.15–0.98	⁴² Ca	0.656–0.640	¹⁷⁶ Hf	5.271–5.206
		⁴³ Ca	0.146–0.131	¹⁷⁷ Hf	18.606–18.593
N		⁴⁴ Ca	2.130–2.057	¹⁷⁸ Hf	27.297–27.278
¹⁴ N	99.890–99.652	⁴⁶ Ca	0.0046–0.0031	¹⁷⁹ Hf	13.630–13.619
¹⁵ N	0.411–0.348	⁴⁸ Ca	0.200–0.179	¹⁸⁰ Hf	35.100–35.076
O		V		Pb	
¹⁶ O	99.7384–99.7756	⁵⁰ V	0.2502–0.2487	²⁰⁴ Pb	1.65–1.04
¹⁷ O	0.0399–0.0367	⁵¹ V	99.7513–99.7498	²⁰⁶ Pb	27.48–20.84
¹⁸ O	0.2217–0.1877			²⁰⁷ Pb	23.65–17.62
		Cu		²⁰⁸ Pb	56.21–51.28
Ne		⁶³ Cu	69.24–68.98		
²⁰ Ne	90.514–88.47	⁶⁵ Cu	31.02–30.76	U	
²¹ Ne	1.71–0.266			²³⁴ U	0.0059–0.0050
²² Ne	9.96–9.20	Sr		²³⁵ U	0.7202–0.7198
		⁸⁴ Sr	0.58–0.55	²³⁸ U	99.2752–99.2739
		⁸⁶ Sr	9.99–9.75		
		⁸⁷ Sr	7.14–6.94		
		⁸⁸ Sr	82.75–82.29		

2.5.3

Isotope Patterns of Naturally Occurring Elements



The mass of the most abundant isotope is given under the symbol of the element. The lightest isotope is shown at the left end of the x axis.

2.5.4 Calculation of Isotope Distributions

The characteristic abundance patterns resulting from the combination of more than one polyisotopic element can be calculated from the relative abundances of the different isotopes. The following polynomial expression gives the isotope distribution of a polyisotopic molecule:

$$\{p_{i1} A^0 + p_{i2} A^{(m_{i2} - m_{i1})} + p_{i3} A^{(m_{i3} - m_{i1})} + \dots\}^{n_i} \times \\ \{p_{j1} A^0 + p_{j2} A^{(m_{j2} - m_{j1})} + p_{j3} A^{(m_{j3} - m_{j1})} + \dots\}^{n_j} \times \{ \dots$$

where p_{ix} is the relative abundance of the x th isotope of element i , the mass of the x th isotope of the element i is given by m_{ix} , and the exponent n_i stands for the number of atoms of the element i in the molecule. The expansion of this polynomial expression after inserting the p_{ix} and m_{ix} values for all the isotopes 1, 2, 3, ... of the elements i, j, \dots of a given molecule yields an expression that represents the isotope distribution:

$$w_0 A^0 + w_r A^r + w_s A^s + w_t A^t + \dots$$

where the values of $w_0, w_r, w_s, w_t, \dots$ are the relative abundances of $M^{+\cdot}, [M+r]^{+\cdot}, [M+s]^{+\cdot}, [M+t]^{+\cdot}, \dots$, respectively. The use of $A^{(m_{ix} - m_{i1})}$ allows to determine the values of r, s, t, \dots simply by expanding the general polynomial. A numerical value for A , which has no intrinsic meaning, is never needed.

For example, for CBr_2Cl_2 , the above equation gives rise to the following expression:

$$\{p_{12\text{C}} A^0 + p_{13\text{C}} A^{(m_{13\text{C}} - m_{12\text{C}})}\} \times \\ \{p_{79\text{Br}} A^0 + p_{81\text{Br}} A^{(m_{81\text{Br}} - m_{79\text{Br}})}\}^2 \times \\ \{p_{35\text{Cl}} A^0 + p_{37\text{Cl}} A^{(m_{37\text{Cl}} - m_{35\text{Cl}})}\}^2$$

For sufficient resolution, $(m_{ix} - m_{i1})$ and $(m_{jx} - m_{j1})$ differ from one another. This results in very complex isotope patterns even for very small molecules. Thus, owing to the occurrence of ^{12}C , ^{13}C , ^{79}Br , ^{81}Br , ^{35}Cl , and ^{37}Cl , there are 18 signals for CBr_2Cl_2 . However, the limited resolution of most real life experiments makes many pairs of $(m_{ix} - m_{i1})$ and $(m_{jx} - m_{j1})$ indistinguishable within experimental error, significantly reducing the number of separate peaks. For example, at unit resolution, one obtains $(m_{81\text{Br}} - m_{79\text{Br}}) = (m_{37\text{Cl}} - m_{35\text{Cl}}) = 2$. Consequently, the expression for BrCl becomes:

$$\{p_{79\text{Br}} A^0 + p_{81\text{Br}} A^2\} \times \{p_{35\text{Cl}} A^0 + p_{37\text{Cl}} A^2\} =$$

$$p_{79\text{Br}} p_{35\text{Cl}} A^0 + (p_{79\text{Br}} p_{37\text{Cl}} + p_{81\text{Br}} p_{35\text{Cl}}) A^2 + p_{37\text{Cl}} p_{81\text{Br}} A^4$$

This shows that at unit resolution, BrCl gives rise to only 3 peaks (M^{+} , $[M+2]^{+}$, $[M+4]^{+}$) rather than to 4 peaks, as they are expected for very high resolution.

Often, the contribution of isotopes of low abundance can be neglected without sacrificing much precision. For example, the effect of ^2H on isotope patterns is usually insignificant. Also, ^{13}C is often negligible when focussing on peaks of the series $[M+2n]^{+}$, which then results in patterns that are characteristic for halogens, sulfur, and silicon. In large molecules, however, isotopes of low abundance cannot be neglected. For example, in the case of buckminster fullerene (C_{60}), not only M^{+} (relative intensity, 100%) and $[M+1]^{+}$ (66.72%) but also $[M+2]^{+}$ (21.89%), $[M+3]^{+}$ (4.71%), and even $[M+4]^{+}$ (0.75%) are quite significant ions.

As shown above, typical isotope patterns can be readily calculated manually by applying the general equation and neglecting isotopes of low abundance. The outlined procedure can also be easily implemented and evaluated with generic computer software that allows simple calculations. Dedicated and user-friendly programs that already contain the necessary isotope abundances and masses are available. Incidentally, because the use of the above equation for systems with 1000 or more polyisotopic atoms results in excessive calculation times, more efficient but somewhat more complicated algorithms have been developed for implementation in dedicated programs [4]. Typical isotope patterns are given on the following pages.

2.5.5

Isotopic Abundances of Various Combinations of Chlorine, Bromine, Sulfur, and Silicon

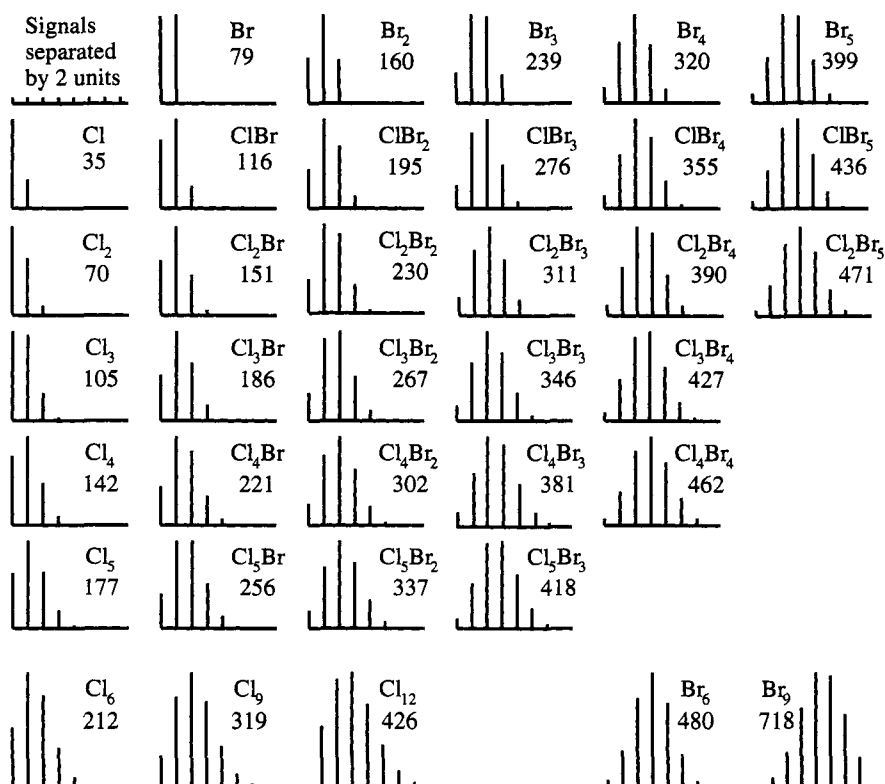
Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance
Cl ₁	35	100	Br ₁	79	100	S ₁	32	100
	37	31.98		81	97.88		33	0.79
Cl ₂	70	100	Br ₂	158	51.09	S ₂	34	4.43
	72	63.96		160	100		64	100
	74	10.23		162	48.93		65	1.58
Cl ₃	105	100	Br ₃	237	34.05	S ₃	66	8.87
	107	95.93		239	100		68	0.24
	109	30.67		241	97.89		96	100
	111	3.27		243	31.94		97	2.37
Cl ₄	140	77.96	Br ₄	316	17.40	S ₄	98	13.31
	142	100		318	68.09		99	0.21
	144	47.82		320	100		100	0.66
	146	10.19		322	65.26		128	100
	148	0.82		324	15.96		129	3.16
Cl ₅	175	62.53	Br ₅	395	10.43	S ₅	130	17.76
	177	100		397	51.09		131	0.42
	179	63.94		399	100		132	1.27
	181	20.45		401	97.94		160	100
	183	3.28		403	47.89		161	3.94
	185	0.21		405	9.38		162	22.22
Cl ₆	210	52.12	Br ₆	474	5.32	S ₆	163	0.70
	212	100		476	31.26		164	2.08
	214	79.95		478	76.62		166	0.11
	216	34.08		480	100		192	100
	218	8.21		482	73.38		193	4.73
	220	1.05		484	28.73		194	26.68
	222	0.06		486	4.68		195	1.05
Si ₁	28	100	Si ₂	56	100	Si ₃	196	3.09
	29	5.06		57	10.13		198	0.20
	30	3.36		58	6.98		84	100
				59	0.34		85	15.19
				60	0.11		86	10.85
							87	1.03
							88	0.36

Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance
Cl ₁ Br ₁	114	76.70	Cl ₁ Br ₂	193	43.83	Cl ₁ Br ₃	272	26.15
	116	100		195	100		274	85.22
	118	24.46		197	69.83		276	100
				199	13.66		278	48.90
Cl ₁ Br ₄	351	14.26	Cl ₂ Br ₁	149	61.35		Cl ₂ Br ₂	228
	353	60.41		151	100	230		100
	355	100		153	45.67	232		89.63
	357	79.93		155	6.38	234		31.89
	359	30.39			236	3.90		
	361	4.25						
Cl ₃ Br ₁	184	51.12	Cl ₃ Br ₂	263	31.35	Cl ₄ Br ₁	219	43.79
	186	100		265	92.01		221	100
	188	65.22		267	100		223	83.86
	190	17.73		269	50.01		225	33.42
	192	1.74		271	11.70		227	6.93
Cl ₄ Br ₂	298	24.14	Cl ₄ Br ₃	377	13.63	Cl ₄ Br ₄	456	7.43
	300	78.63		379	57.78		458	38.40
	302	100		381	100		460	83.70
	304	63.54		383	91.19		462	100
	306	21.54		385	47.13		464	71.37
	308	3.73		387	14.03		466	31.11
	310	0.26		389	2.22		468	8.10
Cl ₁ S ₁	67	100	Cl ₁ S ₂	99	100	Cl ₂ S ₁	102	100
	68	0.79		100	1.58		103	0.79
	69	36.41		101	40.85		104	68.39
	70	0.25		102	0.57		105	0.50
	71	1.44		103	3.08		106	13.08
Cl ₂ S ₂	134	100	Cl ₃ S ₁	137	99.64	Cl ₃ S ₂	169	95.42
	135	1.58		138	0.79		170	1.51
	136	72.82		139	100		171	100
	137	1.08		140	0.75		172	1.51
	138	16.14		141	34.82		173	37.62
	139	0.21		142	0.24		174	0.53
	140	1.06		143	4.63		175	5.94
		145	0.15	177	0.35			

Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance	Ele- ments	Mass	Relative abun- dance
Cl_1Si_1	63	100	Cl_2Si_1	98	100	Cl_3Si_1	133	100
	64	5.06		99	5.06		134	5.06
	65	35.34		100	67.32		135	99.30
	66	1.62		101	3.24		136	4.86
	67	1.07		102	12.38		137	33.90
				103	0.52		138	1.55
				104	0.34		139	4.30

2.5.6

Isotope Patterns of Combinations of Cl and Br



The signals are separated by 2 mass units, and the combination of the lightest isotopes is given on the left side of the x axis. The mass for the most abundant signal is shown under the symbol of the element. See Chapter 2.5.5 for exact abundances of many of these combinations.

2.5.7

Indicators of the Presence of Heteroatoms

In low-resolution mass spectra, one often observes characteristic isotope patterns, specific masses of fragment ions, and characteristic mass differences (Δm) between the molecular ion ($M^{+\cdot}$) and fragment ions (Frag^+), or between fragment ions. High resolution mass spectra can be used to confirm the elemental composition provided that the resolution is sufficient to discriminate alternative compositions. Moreover, tandem mass spectrometry (also called MS/MS) may be used to identify heteroatom-characteristic losses from parent or fragment ions.

- Indication of O: Δm 17 from $M^{+\cdot}$, in N-free compounds
 Δm 18 from $M^{+\cdot}$
 Δm 18 from Frag^+ , particularly in aliphatic compounds
 Δm 28, 29 from $M^{+\cdot}$ for aromatic compounds
 Δm 28 from Frag^+ for aromatic compounds
 m/z 15, relatively abundant
 m/z 19
 m/z 31, 45, 59, 73, ... + $(14)_n$
 m/z 32, 46, 60, 74, ... + $(14)_n$
 m/z 33, 47, 61, 75, ... + $(14)_n$ for $2 \times \text{O}$, in absence of S
 m/z 69 for aromatic compounds meta-disubstituted by oxygen
- Indication of N: $M^{+\cdot}$ odd-numbered (indicates odd number of N in $M^{+\cdot}$)
 Large number of even-numbered fragment ions
 Δm 17 from $M^{+\cdot}$ or Frag^+ , in O-free compounds
 Δm 27 from $M^{+\cdot}$ or Frag^+ , for aromatic compounds or nitriles
 Δm 30, 46 for nitro compounds
 m/z 30, 44, 58, 72, ... + $(14)_n$ for aliphatic compounds
- Indication of S: Isotope peak $[M+2]^{+\cdot} \geq 5\% M^{+\cdot}$
 Δm 33, 34, 47, 48, 64, 65 from $M^{+\cdot}$
 Δm 34, 48, 64 from Frag^+
 m/z 33, 34, 35
 m/z 45 in O-free compounds
 m/z 47, 61, 75, 89, ... + $(14)_n$ unless compound with $2 \times \text{O}$
 m/z 48, 64 for S-oxides
- Indication of F: Δm 19, 20, 50 from $M^{+\cdot}$
 Δm 20 from Frag^+
 m/z 20
 m/z 57 without m/z 55 in aromatics
- Indication of Cl: Isotope peak $[M+2]^{+\cdot} \geq 33\% M^{+\cdot}$
 Δm 35, 36 from $M^{+\cdot}$
 Δm 36 from Frag^+
 m/z 35/37, 36/38, 49/51

Indication of Br: Isotope peak $[M+2]^+ \geq 98\% M^+$

Δm 79, 80 from M^+

Δm 80 from Frag^+

m/z 79/81, 80/82

Indication of I: Isotope peak $[M+1]^+$ of very low abundance at relatively high mass

Δm 127 from M^+

Δm 127, 128 from Frag^+

m/z 127, 128, 254

Indication of P: m/z 47 in compounds free of S or $2 \times O$

m/z 99 without isotope peak at m/z 100 in alkyl phosphates

2.5.8

Rules for Determining the Relative Molecular Weight (M_r)

The molecular ion ($M^{+\cdot}$) is defined as the ion that comprises the most abundant isotopes of the elements in the molecule. Interestingly, the lightest isotopes of most elements that frequently occur in organic compounds and their common salts (H, C, N, O, F, Si, P, S, Cl, As, Br, I, Na, Mg, Al, K, Ca, Rb, Cs) are also the most abundant ones. Notable exceptions are B, Li, Se, Sr, and Ba.

$M^{+\cdot}$ is always accompanied by isotope peaks. Their relative abundance depends on the number and kind of the elements present and their natural isotopic distribution. The abundance of $[M^{+\cdot}+1]$ indicates the maximum number of carbon atoms (C_{\max}) according to the following relationship:

$$C_{\max} = 100 [M^{+\cdot}+1] / (1.1 [M^{+\cdot}])$$

$[M^{+\cdot}+2]$ and higher masses indicate the number and kind of elements that have a relatively abundant isotope two mass units heavier (such as S, Si, Cl, Br).

$M^{+\cdot}$ is always an even number if the molecule contains only elements for which the atomic mass and valence are both even-numbered or both odd-numbered (such as H, C, O, S, Si, P, F, Cl, Br, I). In the presence of other elements, $M^{+\cdot}$ becomes an odd number unless the elements are present in an even number (this holds for N, ^{13}C , ^2H).

$M^{+\cdot}$ can only form fragment ions of masses that differ from that of the molecular ion by chemically logical values (Δm). In this context, chemically illogical differences are $\Delta m = 3$ (in the absence of $\Delta m = 1$) to $\Delta m = 14$, $\Delta m = 21$ (in the absence of $\Delta m = 1$) to $\Delta m = 24$, $\Delta m = 37$, 38 and all Δm less than the mass of an element of characteristic isotope pattern in cases where the same isotope pattern is not retained in the fragment ion.

$M^{+\cdot}$ of a compound must contain all elements (and the maximum number of each) that are shown to be present in the fragment ions.

If ionization is performed by electron impact, $M^{+\cdot}$ is the ion with the lowest appearance potential.

If a pure sample flows into the ion source through a molecular leak, $M^{+\cdot}$ exhibits the same effusion rate as can be determined from the fragment ions. The abundance of $M^{+\cdot}$ is proportional to the sample pressure in the ion source.

For polar compounds, $[M+H]^+$ is often observed in mass spectra obtained not only with fast atom bombardment and atmospheric pressure chemical ionization but also with electron impact ionization. In this latter case, the abundance of $[M+H]^+$ changes in proportion to the square of the sample pressure in the ion source.

In the absence of a signal for $M^{+\cdot}$, the molecular weight must have a value that shows a logical and reasonable mass difference, Δm , to all the observed fragment ions.

2.5.9

Homologous Mass Series as Indications of Structural Type

Certain sequences of intensity maxima in the lower mass range and the masses of unique signals are often characteristic of a particular compound type. The intensity distribution of such ion series is in general smooth. Therefore, abrupt changes (maxima and minima) are of structural significance. The ion or ion series that is most indicative of a particular compound type is set in *italics*.

Mass values m/z	Elemental composition	Compound types
12 + 14m	C_nH_{2n-2}	alkenes, monocycloalkanes, alkynes, dienes, cycloalkenes, polycyclic alicyclics, cyclic alcohols
13 + 14m	C_nH_{2n-1}	alkanes, alkenes, <i>monocycloalkanes</i> , alkynes, dienes, cycloalkenes, polycyclic alicyclics, alcohols, alkyl ethers, cyclic alcohols, cycloalkanones, aliphatic acids, esters, lactones, thiols, sulfides, glycols, glycol ethers, alkyl chlorides
	$C_nH_{2n-3}O$	cycloalkanones
14 + 14m	C_nH_{2n}	alkanes, alkenes, monocycloalkanes, polycyclic alicyclics, alcohols, alkyl ethers, thiols, sulfides, alkyl chlorides
	$C_nH_{2n-2}O$	cycloalkanones
15 + 14m	C_nH_{2n+1}	<i>alkanes</i> , alkenes, monocycloalkanes, alkynes, dienes, cycloalkenes, polycyclic alicyclics, alkanones, alkanals, glycols, glycol ethers, alkyl chlorides, acid chlorides
	$C_nH_{2n-1}O$	alkanones, alkanals, <i>cyclic alcohols</i> , acid chlorides
16 + 14m	$C_nH_{2n}O$	<i>alkanones</i> , <i>alkanals</i>
	$C_nH_{2n+2}N$	<i>alkyl amines</i> , <i>aliphatic amides</i>
	$C_nH_{2n}NO$	aliphatic amides
17 + 14m	$C_nH_{2n+1}O$	<i>alcohols</i> , <i>alkyl ethers</i> , aliphatic acids, esters, lactones, glycols, glycol ethers
	$C_nH_{2n-1}O_2$	aliphatic acids, esters, lactones
18 + 14m	$C_nH_{2n}O_2$	<i>aliphatic acids</i> , <i>esters</i> , <i>lactones</i>

Mass values m/z	Elemental composition	Compound types
19 + 14m	$C_nH_{2n+3}O$	alcohols, alkyl ethers
	$C_nH_{2n+1}O_2$	aliphatic acids, esters, lactones
	$C_nH_{2n+1}O_2$	<i>glycols, glycol ethers</i>
	$C_nH_{2n+1}S$	<i>thiols, sulfides</i>
20 + 14m	$C_8H_8 + C_nH_{2n}$	alkylbenzenes
	$C_nH_{2n+2}O_2$	glycols, glycol ethers
	$C_nH_{2n+2}S$	thiols, sulfides
21 + 14m	$C_7H_7 + C_nH_{2n}$	alkylbenzenes
	C_7H_5O	aryl ketones
	$C_nH_{2n}Cl$	<i>alkyl chlorides</i>
	$C_nH_{2n}COCl$	acid chlorides
22 + 14m	$C_6H_6N + C_nH_{2n}$	alkylanilines
	C_nH_{2n-6}	polycyclic alicyclics
23 + 14m	C_nH_{2n-5}	polycyclic alicyclics
24 + 14m	C_nH_{2n-4}	polycyclic alicyclics
25 + 14m	C_nH_{2n-3}	<i>alkynes, dienes, cycloalkenes</i> , polycyclic alicyclics
39, 52±1, 64±1, 76±2, 91±1	$C_nH_n±1$	alkylbenzenes, aromatic hydrocarbons, phenols, aryl ethers, aryl ketones

2.5.10

Mass Correlation Table

Note: As long as it makes sense chemically, CH₂, CH₄, CH₃O, and O₂ in the formulae of the second column may be replaced by N, O, P, and S, respectively (M: molecular mass).

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
1		[M+1] ⁺ , [M-1] ⁻	particularly in FAB spectra, in which M±1 occurs even for moderately basic and acidic compounds, but intensive M ⁺ without M±1 is unusual
7	Li ⁺	[M+7] ⁺ [M-7] ⁻	in FAB spectra in the presence of Li ⁺ in FAB spectra of organic Li ⁺ salts
12	C ⁺		
13	CH ⁺		
14	CH ₂ ⁺ , N ⁺ , N ₂ ⁺⁺ , CO ⁺⁺		
15	CH ₃ ⁺	[M-15] ⁺ (CH ₃)	nonspecific; abundant: methyl, <i>N</i> -ethylamines
16	O ⁺ , NH ₂ ⁺ , O ₂ ⁺⁺	[M-16] ⁺ (CH ₄) (O) (NH ₂)	methyl (rare) nitro compounds, sulfones, epoxides, <i>N</i> -oxides primary amines
17	OH ⁺ , NH ₃ ⁺	[M-17] ⁺ (OH) (NH ₃)	acids (especially aromatic acids), hydroxylamines, <i>N</i> -oxides, nitro compounds, sulfoxides, tertiary alcohols primary amines
18	H ₂ O ⁺ , NH ₄ ⁺	[M-18] ⁺ (H ₂ O)	nonspecific; abundant: alcohols, some acids, aldehydes, ketones, lactones, cyclic ethers O indicator

Mass	Ion	Product ion and composition of the neutral particle lost		Substructure or compound type	
19	H_3O^+ , F^+	$[\text{M}-19]^+$	(F)	fluorides	F indicator
20	HF^+ , Ar^{++} , $\text{CH}_2\text{CN}^{++}$	$[\text{M}-20]^+$	(HF)	fluorides	F indicator
21	$\text{C}_2\text{H}_2\text{O}^{++}$				
22	CO_2^{++}				
23	Na^+	$[\text{M}+23]^+$		in FAB spectra in the presence of Na^+ ; sometimes strong even if Na^+ is only an impurity	
		$[\text{M}-23]^-$		in FAB spectra of organic Na^+ salts	
24	C_2^+				
25	C_2H^+	$[\text{M}-25]^+$	(C_2H)	terminal acetylenyl	
26	C_2H_2^+ , CN^+	$[\text{M}-26]^+$	(C_2H_2) (CN)	aromatics nitriles	
27	C_2H_3^+ , HCN^+	$[\text{M}-27]^+$	(C_2H_3) (HCN)	terminal vinyl, some ethyl esters and <i>N</i> -ethylamides, ethyl phosphates aromatic N, nitriles	
28	C_2H_4^+ , CO^+ , N_2^+ , HCNH^+	$[\text{M}-28]^+$	(C_2H_4) (CO) (N_2)	nonspecific; abundant: cyclohexenes, ethyl esters, propyl ketones, propyl-substituted aromatics aromatic O, quinones, lactones, lactams, unsaturated cyclic ketones, allyl aldehydes diazocompounds; air (intensity 3.7 times larger than for O_2^+ , m/z 32)	
29	C_2H_5^+ , CHO^+	$[\text{M}-29]^+$	(C_2H_5) (CHO)	nonspecific; abundant: ethyl phenols, furans, aldehydes	

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
30	CH ₂ O ⁺ , CH ₂ NH ₂ ⁺ , NO ⁺ , C ₂ H ₆ ⁺ , BF ⁺ , N ₂ H ₂ ⁺ N indicator	[M-30] ⁺ (C ₂ H ₆) (CH ₂ O) (NO)	ethylalkanes, polymethyl compounds cyclic ethers, lactones, primary alcohols nitro and nitroso compounds
31	CH ₃ O ⁺ , CH ₃ NH ₂ ⁺ , CF ⁺ , N ₂ H ₃ ⁺ O indicator	[M-31] ⁺ (CH ₃ O) (CH ₃ NH ₂) (N ₂ H ₃)	methyl esters, methyl ethers, primary alcohols N-methylamines hydrazides
32	O ₂ ⁺ , CH ₃ OH ⁺ , N ₂ H ₄ ⁺ , S ⁺ O indicator	[M-32] ⁺ (O ₂) (CH ₃ OH) (S)	cyclic peroxides; air (intensity 3.7 times smaller than for N ₂ ⁺ , m/z 28) methyl esters, methyl ethers sulfides (together with isotope signal for ³⁴ S)
33	CH ₃ OH ₂ ⁺ , SH ⁺ , CH ₂ F ⁺	[M-33] ⁺ (SH) (CH ₃ + H ₂ O) (CH ₂ F)	nonspecific (together with isotope signal for ³⁴ S) S indicator nonspecific; O indicator fluoromethyl
34	SH ₂ ⁺	[M-34] ⁺ (SH ₂) (OH + OH)	nonspecific (together with isotope signal for ³⁴ S) S indicator nitro compounds
35	SH ₃ ⁺ , Cl ⁺	[M-35] ⁺ (Cl) (OH + H ₂ O)	chloro compounds (together with isotope signal for ³⁷ Cl) nitro compounds 2 × O indicator
36	HCl ⁺ , C ₃ ⁺	[M-36] ⁺ (HCl) (H ₂ O + H ₂ O)	chloro compounds 2 × O indicator
37	C ₃ H ⁺ ³⁷ Cl ⁺		chloro compounds (together with isotope signal for ³⁵ Cl)

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
38	$C_3H_2^{+}$		
39	$C_3H_3^+$ K^+	$[M-39]^{+}$ (C_3H_3) $[M+39]^+$ $[M-39]^-$	aromatics in FAB spectra in the presence of K^+ ; sometimes strong even if K^+ is only an impurity in FAB spectra of organic K^+ salts
40	$C_3H_4^{+}$, CH_2CN^+ , Ar^+	$[M-40]^{+}$ (CH_2CN)	cyanomethyl
41	$C_3H_5^+$, CH_3CN^+	$[M-41]^{+}$ (C_3H_5) (CH_3CN)	alicyclics (especially polyalicyclics), alkenes 2-methyl-N-aromatics, N-methylanilines
42	$C_3H_6^{+}$, $C_2H_2O^{+}$, CON^+ , $C_2H_4N^+$	$[M-42]^{+}$ (C_3H_6) (C_2H_2O)	nonspecific; abundant: propyl esters, butyl ketones, butylaromatics, methylcyclohexenes acetates (especially enol acetates), acetamides, cyclohexenones, α,β -unsaturated ketones
43	$C_3H_7^+$, $C_2H_3O^+$, $CONH^+$	$[M-43]^{+}$ (C_3H_7) (CH_3CO)	nonspecific; abundant: propyl, alicyclics, cycloalkanones, cycloalkylamines, cycloalkanols, butylaromatics methyl ketones, acetates, aromatic methyl ethers
44	CO_2^{+} , $C_2H_6N^+$, $C_2H_4O^{+}$, CS^+ , $C_3H_8^{+}$, CH_4Si^+	$[M-44]^{+}$ (C_3H_8) (C_2H_6N) (C_2H_4O) (contd.)	propylalkanes N,N-dimethylamines, N-ethylamines cycloalkanols, cyclic ethers, ethylene ketals, aliphatic aldehydes (McLafferty rearrangement)

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
44		(CO ₂)	anhydrides, lactones, carboxylic acids
45	C ₂ H ₅ O ⁺ , C ₂ H ₇ N ⁺ , CHS ⁺ (together with isotope signal for ³⁴ S) O indicator S indicator	[M-45] ⁺ (C ₂ H ₅ O) (CHO ₂) (C ₂ H ₇ N)	ethyl esters, ethyl ethers, lactones, ethyl sulfonates, ethyl sulfones carboxylic acids <i>N,N</i> -dimethylamines, <i>N</i> -ethylamines
46	C ₂ H ₅ OH ⁺ , NO ₂ ⁺	[M-46] ⁺ (C ₂ H ₆ O) (H ₂ O + C ₂ H ₄) (H ₂ O + CO) (NO ₂)	ethyl esters, ethyl ethers, ethyl sulfonates primary alcohols carboxylic acids nitro compounds
47	CH ₃ S ⁺ , CCl ⁺ , C ₂ H ₅ OH ₂ ⁺ , CH(OH) ₂ ⁺ , PO ⁺ 2 × O indicator S indicator P indicator	[M-47] ⁺ (CH ₃ S)	methyl sulfides (together with isotope signal for ³⁴ S)
48	CH ₃ SH ⁺ , CHCl ⁺ , SO ⁺	[M-48] ⁺ (CH ₄ S) (SO)	methyl sulfides sulfoxides, sulfones, sulfonates (together with isotope signal for ³⁴ S)
49	CH ₂ Cl ⁺ , CH ₃ SH ₂ ⁺	[M-49] ⁺ (CH ₂ Cl)	chloromethyl (with corresponding signal for ³⁷ Cl)
50	C ₄ H ₂ ⁺ , CH ₃ Cl ⁺ , CF ₂ ⁺	[M-50] ⁺ (CF ₂)	trifluoromethylaromatics, perfluoroalicyclics
51	C ₄ H ₃ ⁺ , CHF ₂ ⁺		
52	C ₄ H ₄ ⁺		
53	C ₄ H ₅ ⁺		

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
54	$C_4H_6^+$, $C_2H_4CN^+$	$[M-54]^+$ (C_4H_6) (C_2H_4CN)	cyclohexenes cyanoethyl
55	$C_4H_7^+$, $C_3H_3O^+$	$[M-55]^+$ (C_4H_7)	nonspecific; abundant: alicyclics, butyl esters, <i>N</i> -butylamides
56	$C_4H_8^+$, $C_3H_4O^+$	$[M-56]^+$ (C_4H_8) (C_3H_4O)	butyl esters, <i>N</i> -butylamides, pentyl ketones, cyclohexenes, tetralins, pentylaromatics methylcyclohexenones, β -tetralones
57	$C_4H_9^+$, $C_3H_5O^+$, $C_3H_2F^+$	$[M-57]^+$ (C_4H_9) (C_3H_5O)	nonspecific ethyl ketones
58	$C_3H_8N^+$, $C_3H_6O^+$ N indicator O indicator	$[M-58]^+$ (C_4H_{10}) (C_3H_6O)	alkanes α -methylalkanals, methyl ketones, isopropylidene glycols
59	$C_3H_7O^+$, $C_2H_5NO^+$ O indicator	$[M-59]^+$ (C_3H_7O) ($C_2H_3O_2$) (C_3H_9N)	propyl esters, propyl ethers methyl esters amines, amides
60	$C_2H_4O_2^+$, $CH_2NO_2^+$, $C_2H_6NO^+$ O indicator	$[M-60]^+$ (C_3H_8O) ($C_2H_4O_2$) ($CH_3OH + CO$)	propyl esters, propyl ethers acetates methyl esters
61	$C_2H_5O_2^+$, $C_2H_5S^+$ 2 \times O indicator S indicator	$[M-61]^+$ ($C_2H_5O_2$) (C_2H_5S)	glycols, ethylene ketals ethyl sulfides (together with isotope signal for ^{34}S)
62	$C_2H_6O_2^+$, $C_2H_3Cl^+$	$[M-62]^+$ ($C_2H_6O_2$) (C_2H_6S)	methoxymethyl ethers, ethylene glycols, ethylene ketals ethyl sulfides (together with isotope signal for ^{34}S)

Mass	Ion	Product ion and composition of the neutral particle lost	Substructure or compound type
63	$C_5H_3^+$, $C_2H_4Cl^+$, $COCl^+$	$[M-63]^{+•}$ (C_2H_4Cl) ($CO + Cl$)	chloroethyl acid chlorides
64	$C_5H_4^{+•}$, $SO_2^{+•}$, $S_2^{+•}$	$[M-64]^{+•}$ (SO_2) (S_2)	sulfones, sulfonates disulfides (together with isotope signal for ^{34}S)
65	$C_5H_5^+$, $H_2PO_2^+$	$[M-65]^{+•}$ (S_2H) (SO_2H)	disulfides (together with isotope signal for ^{34}S)
66	$C_5H_6^{+•}$ S_2H_2	$[M-66]^{+•}$ (C_5H_6)	cyclopentenenes disulfides (together with isotope signal for ^{34}S)
67	$C_5H_7^+$, $C_4H_3O^+$	$[M-67]^{+•}$ (C_4H_3O)	furyl ketones
68	$C_5H_8^{+•}$, $C_4H_4O^{+•}$, $C_3H_6CN^+$	$[M-68]^{+•}$ (C_5H_8) (C_4H_4O)	cyclohexenes, tetralins cyclohexenones, β -tetralones
69	$C_5H_9^+$, $C_4H_5O^+$, $C_3HO_2^+$, CF_3^+	$[M-69]^{+•}$ (C_5H_9) (CF_3)	alicyclics, alkenes trifluoromethyl
70	$C_5H_{10}^{+•}$ $C_4H_6O^{+•}$ $C_4H_8N^+$		alkanes, alkenes, alicyclics cycloalkanones pyrrolidines

Mass	Ion	Compound type	
71	$C_5H_{11}^+$ $C_4H_7O^+$	alkanes, larger alkyl groups alkanones, alkanals, tetrahydrofurans	
72	$C_4H_8O^{+•}$ $C_4H_{10}N^{+•}$ C_6^+	alkanones, alkanals aliphatic amines perhalogenated benzenes	O indicator N indicator
73	$C_4H_9O^+$ $C_3H_5O_2^+$ $C_3H_9Si^+$	alcohols, ethers, esters acids, esters, lactones trimethylsilyl compounds	O indicator

Mass	Ion	Compound type
74	$C_4H_{10}O^{+}$ $C_3H_6O_2^{+}$	ethers methyl esters of carboxylic acids, α -methyl carboxylic acids
75	$C_3H_7O_2^{+}$ $C_3H_7S^{+}$ $C_2H_7SiO^{+}$	methyl acetals, glycols 2 × O indicator sulfides, thiols (together with isotope signal for ^{34}S) S indicator trimethylsilyloxyl compounds
76	$C_6H_4^{+}$	aromatics
77	$C_6H_5^{+}$ $C_3H_6Cl^{+}$	aromatics chloro compounds
78	$C_6H_6^{+}$ $C_5H_4N^{+}$ $C_3H_7Cl^{+}$	aromatics pyridines chloro compounds
79	$C_6H_7^{+}$ $C_5H_5N^{+}$ Br^{+}	aromatics with H-containing substituents pyridines, pyrroles bromo compounds (together with isotope signal for ^{81}Br)
80	$C_6H_8^{+}$ $C_5H_4O^{+}$ HBr^{+} $C_5H_6N^{+}$	cyclohexenes, polycyclic alicyclics cyclopentenones bromo compounds pyrroles, pyridines
81	$C_6H_9^{+}$ $C_5H_5O^{+}$ $^{81}Br^{+}$	cyclohexanes, cyclohexenyls, dienes furans, pyrans bromo compounds (together with isotope signal for ^{79}Br)
82	$C_6H_{10}^{+}$ $C_5H_6O^{+}$ $C_5H_8N^{+}$ $C_4H_6N_2^{+}$ CCl_2^{+}	cyclohexanes cyclopentenones, dihydropyrans tetrahydropyridines pyrazoles, imidazoles chloro compounds (together with isotope signals at m/z 84 and 86)
83	$C_6H_{11}^{+}$ $C_5H_7O^{+}$	alkenes, alicyclics, monosubstituted alkanes cycloalkanones
84	$C_5H_{10}N^{+}$	piperidines, <i>N</i> -methylpyrrolidines

Mass	Ion	Compound type
85	$C_6H_{13}^+$	alkanes
	$C_5H_9O^+$	alkanones, alkanals, tetrahydropyrans, fatty acid derivatives
	$CClF_2^+$	chlorofluoroalkanes (with isotope signal at m/z 87)
86	$C_5H_{10}O^+$	alkanones, alkanals
	$C_5H_{12}N^+$	aliphatic amines N indicator
87	$C_5H_{11}O^+$	alcohols, ethers, esters O indicator
	$C_4H_7O_2^+$	esters, acids
88	$C_4H_8O_2^+$	ethyl esters of carboxylic acids, α -methyl-methyl esters, α -C ₂ -carboxylic acids
89	$C_4H_9O_2^+$	diols, glycol ethers 2 × O indicator
	$C_4H_9S^+$	sulfides (together with isotope signal for ³⁴ S)
90	$C_7H_6^+$	disubstituted aromatics
91	$C_7H_7^+$	aromatics
	$C_4H_8Cl^+$	alkyl chlorides
92	$C_7H_8^+$	alkylbenzenes
	$C_6H_6N^+$	alkylpyridines
93	$C_6H_5O^+$	phenols, phenol derivatives
	$C_6H_7N^+$	anilines
	CH_2Br^+	bromo compounds
94	$C_6H_6O^+$	phenol esters, phenol ethers
	$C_5H_4NO^+$	pyrrol ketones, pyridone derivatives
95	$C_5H_3O_2^+$	furyl ketones
96	$C_7H_{12}^+$	alicyclics
97	$C_7H_{13}^+$	alicyclics, alkenes
	$C_6H_9O^+$	cycloalkanones
	$C_5H_5S^+$	alkylthiophenes (together with isotope signal for ³⁴ S)
98	$C_6H_{12}N^+$	N-alkylpiperidines

Mass	Ion	Compound type
99	$C_7H_{15}^+$ $C_6H_{11}O^+$ $C_5H_7O_2^+$ $H_4PO_4^+$	alkanes alkanones ethylene ketals alkyl phosphates
104	$C_8H_8^+$ $C_7H_4O^+$	tetralin derivatives, phenylethyl derivatives disubstituted α -ketobenzenes
105	$C_8H_9^+$ $C_7H_5O^+$ $C_6H_5N_2^+$	alkylaromatics benzoyl derivatives diazophenyl derivatives
106	$C_7H_8N^+$	alkylanilines
111	$C_5H_3OS^+$	thiophenoyl derivatives (together with isotope signal for ^{34}S)
115	$C_9H_7^+$ $C_6H_{11}O_2^+$ $C_5H_7O_3^+$	aromatics esters diesters
119	$C_9H_{11}^+$ $C_8H_7O^+$ $C_2F_5^+$ $C_7H_5NO^+$	alkylaromatics tolyl ketones perfluoroethyl derivatives phenyl carbamates
120	$C_7H_4O_2^+$ $C_8H_{10}N^+$	γ -benzopyrones, salicylic acid derivatives pyridines, anilines
121	$C_8H_9O^+$ and $C_7H_5O_2^+$	hydroxybenzene derivatives
127	$C_{10}H_7^+$ $C_6H_7O_3^+$ $C_6H_6NCl^+$ I^+	naphthalenes unsaturated diesters chlorinated <i>N</i> -aromatics iodo compounds
128	$C_{10}H_8^+$ $C_6H_5OCl^+$ HI^+	naphthalenes chlorinated hydroxybenzene derivatives iodo compounds
130	$C_9H_8N^+$ $C_9H_6O^+$	quinolines, indoles naphthoquinones

Mass	Ion	Compound type
131	$C_{10}H_{11}^+$ $C_5H_7S_2^+$ $C_3F_5^+$	tetralins thioethylene ketals (together with isotope signal for ^{34}S) perfluoroalkyl derivatives
135	$C_4H_8Br^+$	alkyl bromides
141	$C_{11}H_9^+$	naphthalenes
142	$C_{10}H_8N^+$	quinolines
149	$C_8H_5O_3^+$	phthalates
152	$C_{12}H_8^{+ \cdot}$	diphenyl aromatics
165	$C_{13}H_9^+$	diphenylmethane derivatives (fluorenyl cation)
167	$C_8H_7O_4^+$	phthalates
205	$C_{12}H_{13}O_3^+$	phthalates
223	$C_{12}H_{15}O_4^+$	phthalates

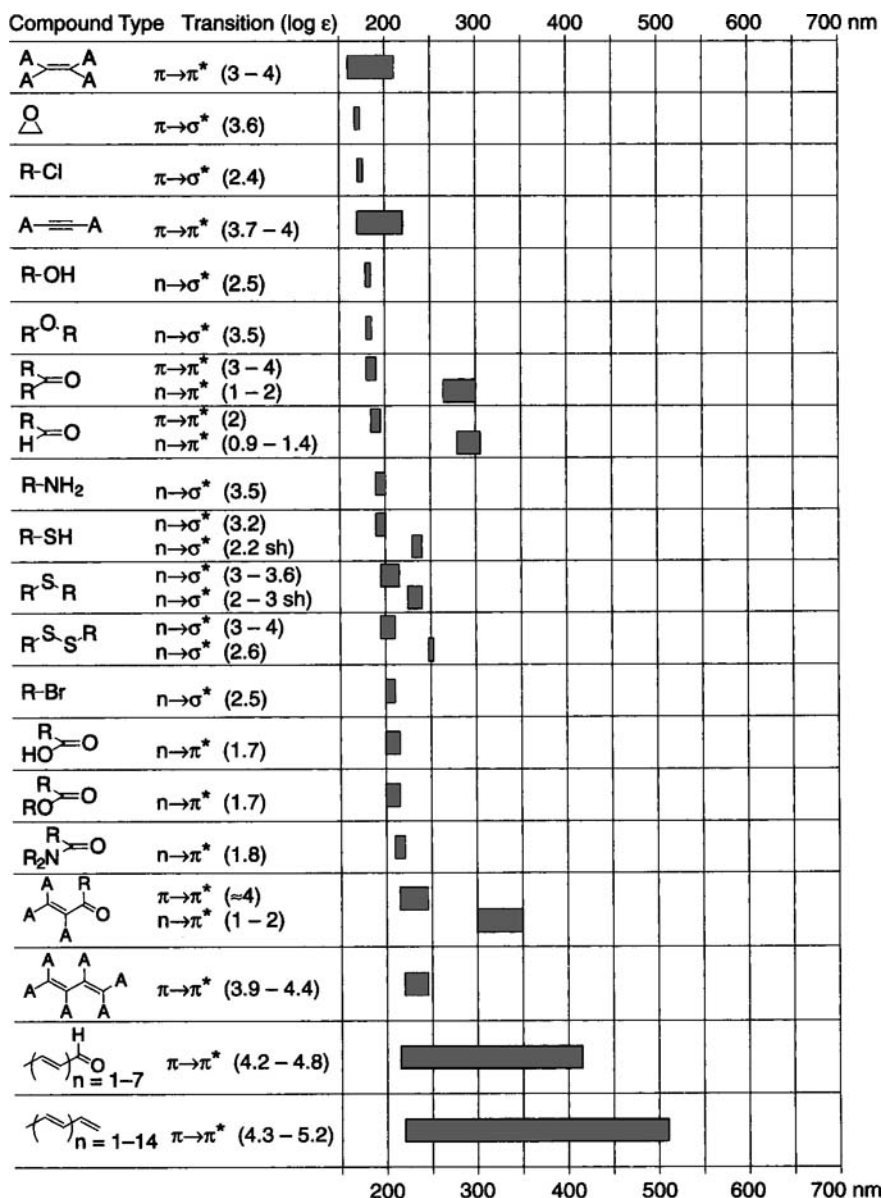
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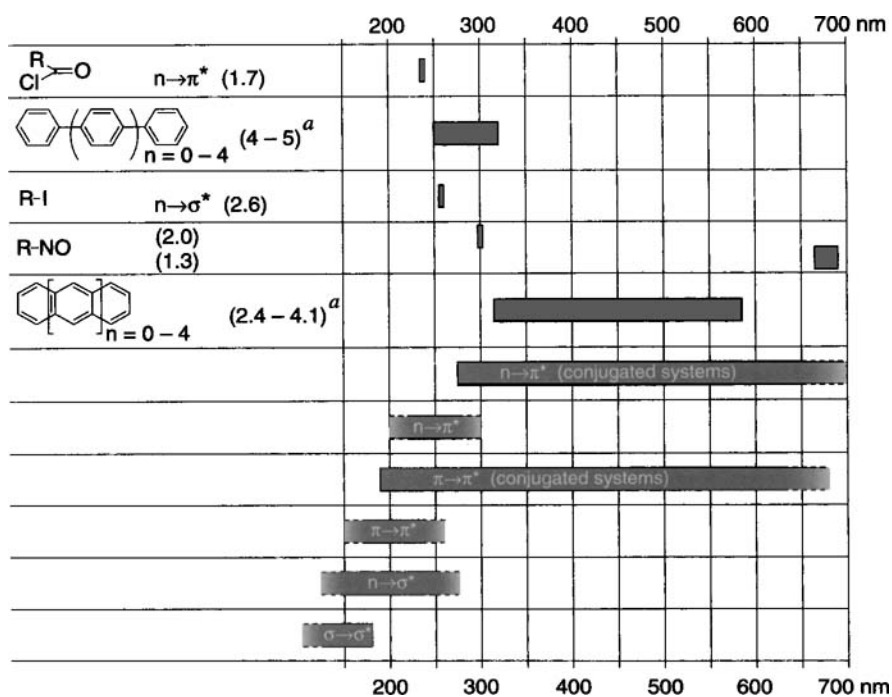
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2.6 UV/Vis Spectroscopy

UV/Vis Absorption Bands of Various Compound Types (A: alkyl or H; R: alkyl; sh: shoulder)





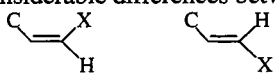
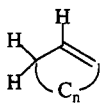
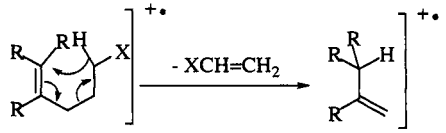
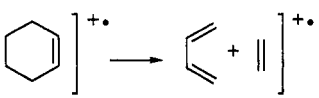
^a longest wavelength absorption maximum

3 Combination Tables

3.1 Alkanes, Cycloalkanes

Assignment	Range	Comments	
CH ₃	5–35 ppm	CH ₃ , CH ₂ , CH, and C can be differentiated by multipulse experiments (DEPT, APT), off-resonance decoupling, 2D CH correlation spectra, or based on relaxation times Lower shift values in three-membered rings	¹³ C NMR
CH ₂	5–45 ppm		
CH	25–60 ppm		
C	30–60 ppm		
CH ₃	0.8–1.2 ppm	Lower shift values in three-membered rings	¹ H NMR
CH ₂	1.1–1.8 ppm		
CH	1.1–1.8 ppm		
CH st	3000–2840 cm ⁻¹	Higher frequency in three-membered rings Doublet for <i>geminal</i> methyl groups In C-(CH ₂) _n -C with n ≥ 4 at ca. 720 cm ⁻¹	IR
CH ₃ δ as	≈1460 cm ⁻¹		
CH ₂ δ	≈1460 cm ⁻¹		
CH ₃ δ sy	≈1380 cm ⁻¹		
CH ₂ γ	770–720 cm ⁻¹		
Molecular ion	m/z 14n + 2	Weak in <i>n</i> -alkanes Very weak in isoalkanes	MS
Fragments		<i>n</i> -Alkanes: local maxima at 14n + 1, intensity variations: smooth, minimum at [M-15] ⁺ Isoalkanes: local maxima at 14n + 1, intensity distribution: irregular (relative maxima due to fragmentation at branching points with charge retention at the most substituted C)	
Rearrangements	m/z 14n m/z 14n - 2	<i>n</i> -Alkanes: unspecific Isoalkanes: elimination of alkanes Monocycloalkanes: elimination of alkanes	
		No absorption above 200 nm	UV

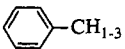
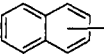
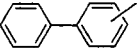
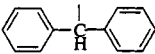
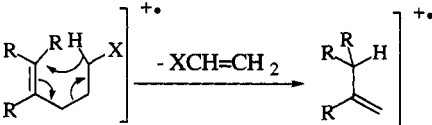
3.2 Alkenes, Cycloalkenes

	Assignment	Range	Comments
¹³C NMR	C=C	100–150 ppm	Considerable differences between Z and E: 
	C–(C=C)	10–60 ppm	
¹H NMR	H–(C=C)	4.5–6.5 ppm	Coupling constants, J : <i>geminal</i> 0–3 Hz, <i>cis</i> 5–12 Hz, <i>trans</i> 12–18 Hz
	CH ₃ –(C=C)	≈1.7 ppm	Coupling constants, ³ J _{CH₂–CH=C} ≈7 Hz
	CH ₂ –(C=C)	≈2.0 ppm	In rings, J smaller:
			 $n=2 \approx 0.5 \text{ Hz}$ $n=3 \approx 1.5 \text{ Hz}$ $n=4 \approx 4.0 \text{ Hz}$
			Long-range coupling constants ⁴ J _{HC–C=CH} 0–2 Hz
IR	H–C(=C) st	3100–3000 cm ^{–1}	
	C=C st	1690–1635 cm ^{–1}	
	H–C(=C) δ oop	1000– 675 cm ^{–1}	
	CH ₂ –(C=C) δ	1440 cm ^{–1}	
MS	Molecular ion	m/z 14n m/z 14n - 2	Alkenes: moderate Monocycloalkenes: medium intensity
	Fragments	14n - 1 14n - 3	Local maxima for alkenes Local maxima for monocyclic alkenes Usually, double bonds cannot be localized
	Rearrange- ments		<i>n</i> -Alkenes: unspecific Specific for:
			
			Cyclohexenes: retro-Diels–Alder reaction: 
UV	C=C π→π*	< 210 nm (log ε 3–4)	Isolated double bonds; for highly substituted double bonds often absorption tail
	(C=C) ₂ π→π*	215–280 nm (log ε 3.5–4.5)	


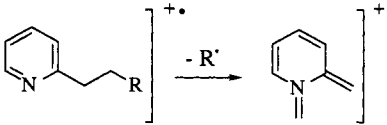
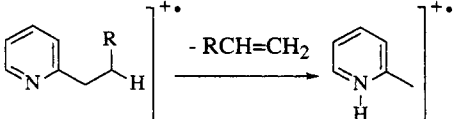
3.3 Alkynes

Assignment	Range	Comments	
$C\equiv C$	65–85 ppm	Coupling constant $^2J_{HC\equiv^{13}C} \approx 50$ Hz; often leading to unexpected signs of signals in DEPT spectra	^{13}C NMR
$C-(C\equiv C)$	0–30 ppm		
$H-(C\equiv C)$	1.5–3.0 ppm	Coupling constants $ J $ $^4J_{CH-C\equiv CH} \approx 3$ Hz $^5J_{CH-C\equiv C-CH} \approx 3$ Hz	1H NMR
$CH_3-(C\equiv C)$	≈ 1.8 ppm		
$CH_2-(C\equiv C)$	≈ 2.2 ppm		
$CH-(C\equiv C)$	≈ 2.6 ppm		
$H-C\equiv C$ st	$3340\text{--}3250\text{ cm}^{-1}$	Sharp, intense	IR
$C\equiv C$ st	$2260\text{--}2100\text{ cm}^{-1}$	Sometimes very weak	
Molecular ion		Weak, for 1-alkynes up to C_7 often absent	MS
Fragments and rearrangements		Vary in extent between alkanes and aromatics	
$C\equiv C \pi \rightarrow \pi^*$	< 210 nm (log ϵ 3.7–4.0)	absorption tail, often a few weak bands < 240 nm	UV

3.4 Aromatic Hydrocarbons

	Assignment	Range	Comments
¹³C NMR	ar C	120–150 ppm	Same ranges for polycyclic aromatic hydrocarbons
	ar CH	110–130 ppm	
	al C–(C ar)	10–60 ppm	
¹H NMR	H–(C ar)	6.5–7.5 ppm	In polycyclic aromatic hydrocarbons up to ≈9 ppm Coupling constants: ³ J _{ortho} ≈7 Hz, ⁴ J _{meta} ≈2 Hz, ⁵ J _{para} <1 Hz
	CH ₃ –(C ar)	≈2.3 ppm	Often line broadening due to long-range coupling with aromatic protons
	CH ₂ –(C ar)	≈2.6 ppm	
	CH–(C ar)	≈2.9 ppm	
IR	ar C–H st	3080–3030 cm ⁻¹	Often multiple bands, weak
	comb	2000–1650 cm ⁻¹	Very weak
	ar C–C st	≈1600 cm ⁻¹ ≈1500 cm ⁻¹ ≈1450 cm ⁻¹	Often split, sometimes not all three bands observable
	ar C–H δ oop	900–650 cm ⁻¹	Strong, frequently multiple bands
MS	Molecular ion		Strong, often base peak
	Fragments	m/z 39, 50–53, 63–65, 75–78 [M–26] ⁺ , [M–39] ⁺ benzylic cleavage	Often doubly charged fragment ions
		 CH ₁₋₃	m/z 90–92
			m/z 127
			m/z 152, 153
Rearrangements			m/z 152, 165
			
UV		≈200–210 nm (log ε ≈4)	In benzene
		≈260 nm (log ε ≈2.4)	and alkylbenzenes

3.5 Heteroaromatic Compounds

Assignment	Range	Comments	
ar C-X	120–160 ppm		¹³ C NMR
ar C-C	100–150 ppm		
H-(C ar)	6–9 ppm	Coupling constants in 6-membered rings similar to those in aromatic hydrocarbons; in 5-membered heteroaromatic rings smaller	¹ H NMR
H-(N ar)	7–14 ppm	Strongly solvent dependent, generally broad	
ar C-H st	3100–3000 cm ⁻¹	Often multiple bands, weak	IR
ar N-H st	3500–2800 cm ⁻¹		
ar C-C st	≈1600 cm ⁻¹ ≈1500 cm ⁻¹ ≈1450 cm ⁻¹		
ar C-H δ oop	1000–650 cm ⁻¹	Often strong, frequently multiple bands	
Molecular ion		Strong, often base peak	MS
Fragments	m/z 39, 50–53, 63–65, 75–78 [M-26] ⁺ , [M-39] ⁺ benzyl-analogous cleavage	Often doubly charged fragment ions	
		 m/z 78	
Rearrangements		Loss of HCN (N-heteroaromatics) Loss of CO (O-heteroaromatics) Loss of CS (S-heteroaromatics) S-Heteroaromatics	
	m/z 45 [CHS] ⁺	 	

cf. UV/Vis Reference Spectra, Chapter 8.5.3.

3.6 Halogen Compounds

	Assignment	Range	Comments
¹³C NMR	al C-F	70–100 ppm	CF ₃ : ≈115 ppm
	(C)=C-F	125–175 ppm	Coupling with ¹⁹ F (isotope abundance,
	C=(C-F)	65–115 ppm	100%; I = 1/2): ¹ J _{CF} 100–300 Hz;
	ar C-F	135–165 ppm	² J _{CF} 10–40 Hz; ³ J _{CF} 5–10 Hz; ⁴ J _{CF} 0–5 Hz
	ar C-(C-F)	105–135 ppm	
	al C-Cl	30–60 ppm	
	(C)=C-Cl	100–150 ppm	
	C=(C-Cl)	100–155 ppm	
	ar C-Cl	120–150 ppm	
	al C-Br	10–45 ppm	
	(C)=C-Br	90–140 ppm	
	C=(C-Br)	90–140 ppm	
	ar C-Br	110–140 ppm	
	al C-I	-20 to +30 ppm	
	(C)=C-I	60–110 ppm	
	C=(C-I)	120–150 ppm	
	ar C-I	85–115 ppm	
¹H NMR	-CH ₂ -F	≈4.3 ppm	Coupling with ¹⁹ F (isotope abundance,
			100%; I = 1/2): ² J _{HF} 40–80 Hz;
			³ J _{HF} 0–50 Hz; ⁴ J _{HF} 0–5 Hz
	-CH ₂ -Cl	≈3.5 ppm	
	-CH ₂ -Br	≈3.4 ppm	
	-CH ₂ -I	≈3.1 ppm	
			Alkenes: <i>geminal</i> protons strongly deshielded
			by all halogens; <i>vicinal</i> protons are shielded
			by F and deshielded by the other halogens
			Aromatics: shielding by F in <i>o</i> - and <i>p</i> -
IR	C-F st	1400–1000 cm ⁻¹	Strong
	C-Cl st	< 850 cm ⁻¹	
	C-Br st	< 700 cm ⁻¹	
	C-I st	< 600 cm ⁻¹	

Assignment	Range	Comments
Molecular ion		For saturated aliphatic halogen compounds often weak, for polyhalogenated compounds often absent
Fragments	m/z 69 [M-50] ⁺ or [Frag-50] ⁺	Characteristic isotope patterns for Cl and Br CF ₃ CF ₂
		$\text{R}-\text{C} \begin{array}{ c} \leftarrow \\ \hline \rightarrow \end{array} \text{-hal} > \text{R} \begin{array}{ c} \leftarrow \\ \hline \rightarrow \end{array} \text{-C-hal}$
Rearrange-ments	[M-20] ⁺ [M-36] ⁺	HF elimination HCl elimination
hal n→π*	≤ 280 nm (log ε ≈ 2.5)	For C-I; for C-Br and C-Cl in general only absorption tail, for C-F no absorption

MS

UV

3.7 Oxygen Compounds

3.7.1 Alcohols and Phenols

	Assignment	Range	Comments
¹³ C NMR	al C-OH	50–100 ppm	Shift with respect to corresponding C-H: $\approx +50$ ppm
	al C-(C-OH)	10–60 ppm	Hardly any shift with respect to C-(C-CH ₃)
	al C-(C-C-OH)	10–60 ppm	Shift with respect to C-(C-C-CH ₃) ≈ -5 ppm
	ar C-OH	135–155 ppm	Shift with respect to C-H $\approx +25$ ppm
	ar C-(C-OH)	100–130 ppm	Shift with respect to C-(C-H): <i>ortho</i> ≈ -13 ppm, <i>meta</i> $\approx +1$ ppm, <i>para</i> ≈ -8 ppm
¹ H NMR	al C-OH	0.5–5 ppm	Position and shape strongly depend on experimental conditions
	ar C-OH	5–8 ppm	
	-CH ₂ -OH	3.5–4.0 ppm	For C-aromatics, shift with respect to CH-(C-H): <i>ortho</i> ≈ -0.6 ppm, <i>meta</i> ≈ -0.1 ppm, <i>para</i> ≈ -0.5 ppm
	-CH-OH	3.8–4.2 ppm	
	ar CH-(C-OH)	6.5–7.0 ppm	
IR	O-H st	3650–3200 cm ⁻¹	Position and shape depend on degree of association; often different bands for H-bonded and free OH
	C-O(H) st	1260–970 cm ⁻¹	Strong
MS	Molecular ion		Aliphatic: weak, often missing for primary and highly branched alcohols; in this case, peaks at highest mass are often due to [M-18] ⁺⁺ or [M-15] ⁺ Aromatic: strong
	Fragments	Aliphatic: m/z 31, 45, 59,... [M-18] ⁺⁺ [M-33] ⁺ [M-46] ⁺⁺ Aromatic: [ar-O] ⁺⁺ [M-28] ⁺⁺ (CO) [M-29] ⁺ (CHO)	Primary: m/z 31 > m/z 45 \approx m/z 59 Secondary, tertiary: local maxima due to α -cleavage: $\text{R}-\overset{\text{R}}{\underset{\text{OH}}{\text{CH}}}-\text{OH} \xrightarrow{+\cdot \quad -\text{R}\cdot} \text{R}-\overset{+}{\text{CH}}=\text{OH}$ Generally accompanied by rearrangement peaks

Assignment	Range	Comments
Rearrange- ments		<p>Aliphatic: elimination of H_2O from $\text{M}^{+\bullet}$ and from products of α-cleavage; elimination of H_2O followed by alkene elimination</p> <p>Unsaturated:</p> <p>vinylcarbinols: spectra similar to those of ketones</p> <p>allyl alcohols: specific, aldehyde elimination:</p> $\left[\text{R}_1-\text{CH}=\text{CH}-\text{CH}(\text{OH})-\text{R}_2 \right]^{+\bullet} \xrightarrow{-\text{R}_2\text{CHO}} \left[\text{R}_1-\text{CH}=\text{CH}-\text{R}_2 \right]^{+\bullet}$ <p>Aromatic: <i>ortho</i> effect with appropriate substituents:</p> $\left[\text{C}_6\text{H}_4(\text{Y})(\text{Z})-\text{O}-\text{H} \right]^{+\bullet} \longrightarrow \left[\text{C}_6\text{H}_4(\text{Y})(\text{Z})=\text{O} \right]^{+\bullet} + \text{H} \cdot / \text{Z} \cdot$ <p>$-\text{Y}-\text{Z}$: $-\text{CO}-\text{OR}$, $-\text{C}-\text{hal}$, $-\text{O}-\text{R}$, and similar</p> <p>Aliphatic: no absorption above 200 nm</p> <p>Aromatic: in alkaline solution, shift to longer wavelength and intensity increase due to deprotonation</p>

UV

3.7.2 Ethers

Assignment	Range	Comments
al C-O	50–100 ppm	Oxiranes: outside the normal range
al C-(C-O)	10–60 ppm	Hardly any shift with respect to C-(C-CH ₃)
al C-(C-C-O)	10–60 ppm	Shift with respect to C-(C-C-CH ₃) \approx -5 ppm
O-C-O	85–110 ppm	
(C)=C-O	115–165 ppm	Shift with respect to (C)=C-C \approx +15 ppm
C=(C-O)	70–120 ppm	Shift with respect to C=(C-C) \approx -30 ppm
ar C-O	135–155 ppm	Shift with respect to C-H \approx +25 ppm
ar C-(C-O)	100–130 ppm	Shift with respect to C-(C-H): <i>ortho</i> \approx -15 ppm, <i>meta</i> \approx +1 ppm, <i>para</i> \approx -8 ppm

¹³C NMR

	Assignment	Range	Comments
¹H NMR	CH ₃ -O	3.3–4.0 ppm	Singlet
	CH ₂ -O	3.4–4.2 ppm	
	O-CH ₂ -O	4.5–6.0 ppm	
	CH-O	3.5–4.3 ppm	
	CH-(O) ₃	≈5–6 ppm	
	H-C(O)=C	5.7–7.5 ppm	Shift with respect to H-C(H)=C ≈ +1.2 ppm
	H-C(=C-O)	3.5–5.0 ppm	Shift with respect to H-C(=C-H) ≈ -1 ppm
	ar CH-(C-O)	6.6–7.6 ppm	
IR	H-C(-O) st	2880–2815 cm ⁻¹	For CH ₃ -O and CH ₂ -O; similar range for amines
	H-CH(-O) ₂ st	2880–2750 cm ⁻¹	Two bands
	C-O-C st as	1310–1000 cm ⁻¹	Strong, sometimes two bands
MS	Molecular ion		Aliphatic: weak, tendency to protonate Aromatic: strong
	Fragments	Aliphatic: m/z 31, 45, 59,... [M-18] ⁺⁺ [M-33] ⁺ [M-46] ⁺⁺	Base peak of aliphatic ethers, generally due to fragmentation of the bond next to the ether bond: $R_1-C-O-R_2 \left[^{++} - R_1^{\bullet} \right] \longrightarrow C=O^+-R_2$ or due to heterolytic cleavage of the C-O bond, especially for polyethers: $R_1-O-R_2 \left[^{++} - R_1-O^{\bullet} \right] \longrightarrow R_2^+$
			Aryl alkyl ethers: preferential loss of the alkyl chain
			Diaryl ethers: preferential loss of CO (28) from M ⁺⁺ and/or [M-H] ⁺ as well as: $ar_1-O-\overset{\curvearrowright}{-}ar_2$
	Rearrange- ments		Aliphatic: elimination of alcohol Aromatic ethyl and higher alkyl ethers: alkene elimination to the phenol: $\left[\text{C}_6\text{H}_5-O-\overset{\text{H}}{\underset{\text{R}}{\text{CH}_2}} \right] ^{++} \xrightarrow{-RCH=CH_2} \left[\text{C}_6\text{H}_5-OH \right] ^{++}$
UV			Aliphatic: no absorption above 200 nm Aromatic: shift to higher wavelength and more intense due to the ether group

3.8 Nitrogen Compounds

3.8.1 Amines

Assignment	Range	Comments	
al C-N	25–80 ppm	Shift with respect to C-H \approx +20 to +30 ppm	¹³ C NMR
al C-(C-N)	10–60 ppm	Shift with respect to C-(C-C) \approx +2 ppm	
al C-(C-C-N)	10–60 ppm	Shift with respect to C-(C-C-C) \approx -2 ppm	
(C)=C-N	120–170 ppm	Shift with respect to (C)=C-C \approx +20 ppm	
C=(C-N)	75–125 ppm	Shift with respect to C=(C-C) \approx -25 ppm	
ar C-N	130–150 ppm	Shift with respect to C-H \approx +20 ppm	
ar C-(C-N)	100–130 ppm	Shift with respect to C-(C-H): <i>ortho</i> \approx -15 ppm, <i>meta</i> \approx +1 ppm, <i>para</i> \approx -10 ppm	
al C-NH	0.5–4.0 ppm		¹ H NMR
ar C-NH	2.5–5.0 ppm		
al or ar N ⁺ H	6.0–9.0 ppm	Often broad	
CH ₃ -N	2.3–3.1 ppm	Singlet	
CH ₂ -N	2.5–3.5 ppm		
CH-N	3.0–3.7 ppm		
CH-N ⁺	3.2–4.0 ppm		
ar CH-(C-N)	6.0–7.5 ppm	For C-aromatics, shift with respect to CH-(C-H): <i>ortho</i> \approx -0.8 ppm, <i>meta</i> \approx -0.2 ppm, <i>para</i> \approx -0.7 ppm	IR
ar CH-(C-N ⁺)	7.5–8.0 ppm	For C-aromatics, shift with respect to CH-(C-H): <i>ortho</i> \approx +0.7 ppm <i>meta</i> \approx +0.4 ppm, <i>para</i> \approx +0.3 ppm	
N-H st	3500–3200 cm ⁻¹	Position depends on extent of association, often different bands for H-bonded and free NH; always at least two bands for NH ₂	
N ⁺ -H st	3000–2000 cm ⁻¹	Broad, similar to COOH band but more structured	
N-H δ	1650–1550 cm ⁻¹	Weak or absent	
N ⁺ -H δ	1600–1460 cm ⁻¹	Often weak	
H-C(-N) st	2850–2750 cm ⁻¹	For CH ₃ (-N) and CH ₂ (-N); similar range for ethers	

	Assignment	Range	Comments
MS	Molecular ion		Odd mass number for odd number of nitrogens Aliphatic: weak, tendency to protonate Aromatic: strong, no tendency to protonate [M+H] ⁺ is often important
	Fragments	Aliphatic: m/z 30, 44, 58,...	Base peak of aliphatic amines generally due to fragmentation of the bond next to the amine bond: $\begin{array}{c} R_1 \\ \\ R_2 - N - CH_2 - R_3 \end{array} \text{ } ^{+\bullet} \xrightarrow{-R_3\bullet} \begin{array}{c} R_1 \\ \\ R_2 - N^+ = CH_2 \end{array}$
	Rearrangements		Elimination of alkenes following amine cleavage: $\begin{array}{c} R_1 \\ \\ R_2 - N^+ = CH_2 \end{array} \longrightarrow R_1 - NH^+ = CH_2$
UV			Aliphatic: no absorption maximum above 200 nm Aromatic: in acidic solution, shift to lower wavelength and decrease in intensity

3.8.2 Nitro Compounds

	Assignment	Range	Comments
¹³ C NMR	al C-NO ₂	55–110 ppm	Shift with respect to C-H ≈ +50 ppm
	al C-(C-NO ₂)	10–50 ppm	Shift with respect to C-(C-C) ≈ -6 ppm
	al C-(CCNO ₂)	10–60 ppm	Shift with respect to C-(C-C-C) ≈ -2 ppm
	ar C-NO ₂	130–150 ppm	Shift with respect to C-H ≈ +20 ppm
	ar C-(C-NO ₂)	120–140 ppm	Shift with respect to C-(C-H): <i>ortho</i> ≈ -5 ppm, <i>meta</i> ≈ +1 ppm, <i>para</i> ≈ +6 ppm
¹ H NMR	al CH-NO ₂	4.2–4.6 ppm	
	ar CH-(C-NO ₂)	7.5–8.5 ppm	For C-aromatics, shift with respect to CH-(C-H): <i>ortho</i> ≈ +1.0 ppm, <i>meta</i> ≈ +0.3 ppm, <i>para</i> ≈ +0.4 ppm
IR	NO ₂ st as	1660–1490 cm ⁻¹	Strong to very strong
	NO ₂ st sy	1390–1260 cm ⁻¹	Strong to very strong

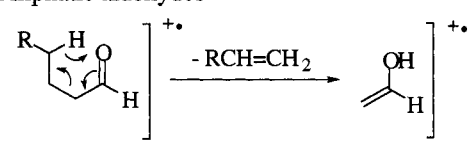
Assignment	Range	Comments	
Molecular ion		Odd mass number for odd number of nitrogens Aliphatic: weak or absent Aromatic: strong	MS
Fragments	[M-16] ⁺ , [M-46] ⁺		
Rearrange- ments	m/z 30, [M-17] ⁺ , [M-30] ⁺ , [M-47] ⁺		
	≈275 nm (log ε <2) Aliphatic ≈350 nm (log ε ≈2) Aromatic		UV

3.9 Thiols and Sulfides

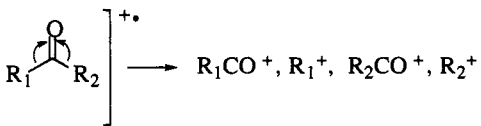
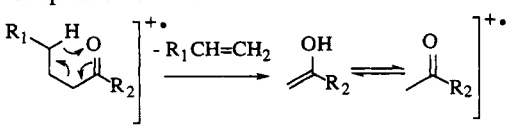
	Assignment	Range	Comments
^{13}C NMR	al C-S	5–60 ppm	No significant shift with respect to C-C
	ar C-S	120–140 ppm	
^1H NMR	al C-SH	1.0–2.0 ppm	<i>Vicinal</i> coupling constant, $J \approx 5\text{--}9$ Hz
	ar C-SH	2.0–4.0 ppm	
	al CH-S	2.0–3.2 ppm	
	ar CH-S	7.0–7.5 ppm	
IR	S-H st	2600–2540 cm^{-1}	Frequently weak
MS	Molecular ion		^{34}S -isotope peak at $[\text{M}+2]^+ \approx 4.5\%$ Aliphatic: intensity higher than for corresponding alcohols and ethers
	Fragments	m/z 47, 61, 75,...	Sulfide cleavage: $\text{R}_1-\text{S}-\text{CH}_2-\text{R}_2 \text{]}^{+\bullet} \xrightarrow{-\text{R}_2^\bullet} \text{R}_1-\overset{+}{\text{S}}=\text{CH}_2$
	Rearrange- ments	m/z 34, 35, 48 $[\text{M}-33]^+$, $[\text{M}-34]^{+\bullet}$	Alkene elimination after sulfide cleavage
UV		<225 nm ($\log \epsilon$ 3–4)	In aliphatic compounds
		220–250 nm ($\log \epsilon$ 2–3)	

3.10 Carbonyl Compounds

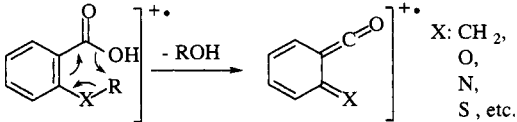
3.10.1 Aldehydes

Assignment	Range	Comments	
CHO	190–205 ppm	Coupling constant $^1J_{CH}$ 172 Hz	^{13}C NMR
al C–(CHO)	30–70 ppm	Coupling constant $^2J_{CH}$ 20–50 Hz	
al C–(C–CHO)	5–50 ppm	Shift with respect to C–(C–CH ₃) \approx -10 ppm	
(C)=C–(CHO)	110–160 ppm		
C=(C–CHO)	110–160 ppm		
ar C–(CHO)	120–150 ppm		
H–(C=O)	9.0–10.5 ppm		1H NMR
al CH–(CHO)	2.0–2.5 ppm	$^3J_{HH}$ 0–3 Hz	
CH=CH–(CHO)	5.5–7.0 ppm	$^3J_{HH}$ \approx 8 Hz	
ar CH–(C–CHO)	7.2–8.0 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> : \approx +0.6 ppm, <i>meta</i> : \approx +0.2 ppm, <i>para</i> : \approx +0.3 ppm	
comb	2900–2700 cm ⁻¹	Two weak bands	IR
C=O st	1765–1645 cm ⁻¹	Aliphatic: \approx 1730 cm ⁻¹ Conjugated: \approx 1690 cm ⁻¹	
Molecular ion		Aliphatic: moderate Aromatic: strong	MS
Fragments	[M-1] ⁺ [M-29] ⁺	For aliphatic aldehydes, only significant up to C ₇	
Rearrange- ments	m/z 44, [M-44] ⁺	Aliphatic aldehydes 	
n \rightarrow π^*	270–310 nm (log $\epsilon \approx$ 1) \geq 207 nm (log $\epsilon \approx$ 4) \geq 250 nm (log $\epsilon >$ 3)	Saturated aldehydes α,β -Unsaturated aldehydes Aromatic aldehydes	UV

3.10.2 Ketones

	Assignment	Range	Comments
¹³ C NMR	C=O	195–220 ppm	
	al C–(C=O)	25–70 ppm	
	al C–(C–C=O)	5–50 ppm	Shift with respect to C–(C–CH ₃) ≈ -6 ppm
	(C)=C–(C=O)	105–160 ppm	
	C=(C–C=O)	105–160 ppm	
	ar C–(C=O)	120–150 ppm	
¹ H NMR	al CH–(C=O)	2.0–3.6 ppm	CH–CO–al 2.0–2.6 ppm CH–CO–ar 2.5–3.6 ppm
	CH=CH–(C=O)	5.5–7.0 ppm	
	ar CH–(C–C=O)	7.2–8.0 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ +0.6 ppm, <i>meta</i> ≈ +0.1 ppm, <i>para</i> ≈ +0.2 ppm
IR	C=O st	1775–1650 cm ⁻¹	Aliphatic: ≈ 1715 cm ⁻¹ Cyclic: ring size ≥ 6: ≈ 1715 cm ⁻¹ ring size < 6: ≥ 1750 cm ⁻¹ Conjugated: ≈ 1690–1665 cm ⁻¹
MS	Molecular ion		Aliphatic: moderate Aromatic: strong
	Fragments		Ketone cleavages:
			
	Rearrange- ments	m/z 44 [M-44] ⁺	Aliphatic ketones 
UV	π→π*	<200 nm (log ε 3–4)	Saturated
	n→π*	250–300 nm (log ε 1–2)	ketones
		≥ 215 nm (log ε ≈ 4)	α,β-Unsaturated ketones
		≥ 245 nm (log ε > 3)	Aromatic ketones

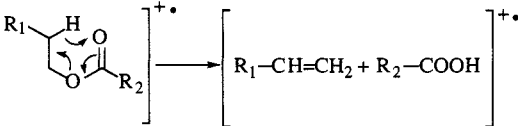
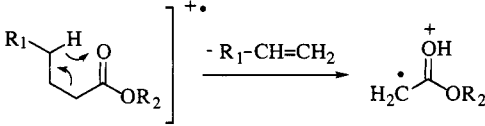
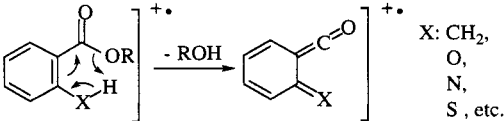
3.10.3 Carboxylic Acids

Assignment	Range	Comments	
COOH	170–185 ppm	In COO ⁻ , shift with respect to COOH: 0 to +8 ppm	¹³ C NMR
al C–(COOH)	25–70 ppm		
al C–(C–COOH)	5–50 ppm	Shift with respect to C–(C–CH ₃) ≈ -6 ppm	
(C)=C–(COOH)	105–160 ppm		
C=(C–COOH)	105–160 ppm		
ar C–(COOH)	120–150 ppm		
COOH	10.0–13.0 ppm	Position and shape strongly depend on experimental conditions	¹ H NMR
al CH–(COOH)	2.0–2.6 ppm		
CH=CH–(COOH)	5.2–7.5 ppm		
ar CH–(C–COOH)	7.2–8.0 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ +0.8 ppm, <i>meta</i> ≈ +0.2 ppm, <i>para</i> ≈ +0.3 ppm	
COO–H st	3550–2500 cm ⁻¹	Broad	IR
C=O st	1800–1650 cm ⁻¹	Aliphatic: ≈ 1715 cm ⁻¹ Conjugated: ≈ 1695 cm ⁻¹ In COO ⁻ two bands: 1580 and 1420 cm ⁻¹	
CO–OH δ oop	≈ 920 cm ⁻¹	For dimers	
Molecular ion		Aliphatic: moderate, strong for long chains, tendency to protonate Aromatic: strong	MS
Fragments	[M–17] ⁺ [M–45] ⁺	Strong for aromatic acids	
Rearrange-ments	m/z 60, 61 [M–18] ⁺	Aliphatic acids Aliphatic acids <i>Ortho</i> effect with aromatic acids:	
			
n→π*	<220 nm (log ε 1–2) ≥193 nm (log ε ≈ 4) ≥230 nm (log ε > 3)	Saturated acids α,β-Unsaturated acids Aromatic acids	UV

3.10.4

Carboxylic Esters and Lactones

	Assignment	Range	Comments
¹³ C NMR	COOR	165–180 ppm	Shift with respect to COOH: -5 to -10 ppm
	al C–(COOR)	20–70 ppm	
	al C–(C–COOR)	5–50 ppm	Shift with respect to C–(C–CH ₃) ≈ -6 ppm
	al C–(OCOR)	50–100 ppm	Shift with respect to C–(OH) +2 to +10 ppm
	(C)=C–(COOR)	105–160 ppm	
	C=(C–COOR)	105–160 ppm	
	(C)=C–(OCOR)	100–150 ppm	
	C=(C–OCOR)	80–130 ppm	
	ar C–(COOR)	120–150 ppm	
	ar C–(OCOR)	100–160 ppm	
¹ H NMR	al CH–(COOR)	2.0–2.5 ppm	CH ₃ COOR ≈ 2.0 ppm; CH ₂ COOR ≈ 2.3 ppm CHCOOR ≈ 2.5 ppm
	al CH–(OCOR)	3.5–5.3 ppm	CH ₃ OCOR ≈ 3.5–3.9 ppm CH ₂ OCOR ≈ 4.0–4.5 ppm CHOCOR ≈ 4.8–5.3 ppm
	CH=CH–(COOR)	5.2–7.5 ppm	Shift with respect to CH=CH–H: <i>geminal</i> ≈ +0.8 ppm, <i>cis</i> ≈ +1.1 ppm, <i>trans</i> : ≈ +0.5 ppm
	C=CH–(OCOR)	6.0–8.0 ppm	Shift with respect to CH=CH–H:
	CH=C–(OCOR)	4.5–6.0 ppm	<i>geminal</i> ≈ +2.1 ppm, <i>cis</i> ≈ -0.4 ppm, <i>trans</i> ≈ -0.6 ppm
	ar CH–(C–COOR)	7.5–8.5 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ +0.7 ppm, <i>meta</i> ≈ +0.1 ppm, <i>para</i> ≈ +0.2 ppm
	ar CH–(C–OCOR)	6.8–7.5 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ -0.2 ppm, <i>meta</i> ≈ 0 ppm, <i>para</i> ≈ -0.1 ppm
IR	C=O st	1745–1730 cm ⁻¹	Strong; range for aliphatic esters Higher wavenumbers for hal–C–COO, COO–C=C, COO–ar, and for small-ring lactones Lower wavenumbers for C=C–COOR and ar–COOR
	C–O st	1330–1050 cm ⁻¹	Mostly two bands, at least one of them strong

Assignment	Range	Comments
Molecular ion		Aliphatic esters: weak, tendency to protonate Aliphatic lactones: medium to weak, tendency to protonate Aromatic esters and lactones: strong
Fragments	$[M - RO]^+$ $[M - ROCO]^+$	Esters Esters Lactones: loss of α -substituents (attached to ether carbon), decarbonylation, for aromatic lactones also double decarbonylation
Rearrangements		Alkene elimination from the alcohol moiety:  $\left[\text{Cyclic ester} \right]^{+\bullet} \longrightarrow \left[R_1-CH=CH_2 + R_2-COOH \right]^{+\bullet}$ <p>Elimination of the alcohol side chain with double hydrogen transfer (for $> C_2$ alcohols)</p> $R_1-COOR_2 \left]^{+\bullet} \longrightarrow R_1-C(=OH)-OH$ <p>Elimination of the alkyl chain of the acid moiety as an alkene</p>  $\left[\text{Ester} \right]^{+\bullet} \xrightarrow{-R_1-CH=CH_2} \left[\text{Carboxylic acid} \right]^{+\bullet}$ <p>Alcohol elimination from <i>ortho</i>-substituted aromatic esters</p>  $\left[\text{ortho-substituted aromatic ester} \right]^{+\bullet} \xrightarrow{-ROH} \left[\text{Quinone-like structure} \right]^{+\bullet}$ <p>X: CH_2, O, N, S, etc.</p>
	$[M-18]^{+\bullet}$	Lactones
$n \rightarrow \pi^*$	<220 nm (log ϵ 1–2) ≥ 193 nm (log $\epsilon \approx 4$) ≥ 230 nm (log $\epsilon > 3$)	Aliphatic esters α, β -Unsaturated esters Aromatic esters

MS

UV

3.10.5

Carboxylic Amides and Lactams

	Assignment	Range	Comments
¹³ C NMR	CONR ₂	165–180 ppm	
	al C–(CONR ₂)	20–70 ppm	
	al C–(C–CONR ₂)	5–50 ppm	Shift with respect to C–(C–CH ₃) ≈ -6 ppm
	al C–(NCOR)	25–80 ppm	Shift with respect to C–(NH) ≈ -1 to -2 ppm
	C=C–(CONR ₂)	105–160 ppm	
	ar C–(CONR ₂)	120–150 ppm	
	ar C–(NCOR)	110–150 ppm	
¹ H NMR	CONH	5–10 ppm	Frequently broad to very broad; splitting due to H–N–C–H coupling often only recognizable in the CH signal
	al CH–(CONR ₂)	2.0–2.5 ppm	
	al CH–(NCOR)	2.7–4.8 ppm	CH ₃ NCOR ≈ 2.7–3.0 ppm; CH ₂ NCOR ≈ 3.1–3.5 ppm; CHNCOR ≈ 3.8–4.8 ppm
	CH=CH–(CONR ₂)	5.2–7.5 ppm	Shift with respect to CH=CH–H: <i>geminal</i> ≈ +1.4 ppm, <i>cis</i> ≈ +1.0 ppm, <i>trans</i> ≈ +0.5 ppm
	C=CH–(NCOR)	6.0–8.0 ppm	Shift with respect to CH=CH–H: <i>geminal</i> ≈ +2.1 ppm, <i>cis</i> ≈ -0.6 ppm, <i>trans</i> ≈ -0.7 ppm
	CH=C–(NCOR)	4.5–6.0 ppm	
	ar CH–C(CONR ₂)	7.5–8.5 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ +0.6 ppm, <i>meta</i> ≈ +0.1 ppm, <i>para</i> ≈ +0.2 ppm
	ar CH–C(NCOR)	6.8–7.5 ppm	For C-aromatics, shift with respect to CH–(C–H): <i>ortho</i> ≈ 0 ppm, <i>meta</i> ≈ 0 ppm, <i>para</i> : ≈ 0 to -0.3 ppm
IR	N–H st	3500–3100 cm ⁻¹	Position and shape depend on extent of association, often different bands for H-bonded and free NH, always at least two bands for NH ₂
	C=O st (amide I)	1700–1650 cm ⁻¹	Strong, range given for amides as well as for δ- and larger lactams, higher wavenumbers for β- and γ-lactams
	N–H δ and N–C=O st sy (amide II)	1630–1510 cm ⁻¹	Often strong, missing for tertiary amides and lactams

Assignment	Range	Comments	
Molecular ion		Aliphatic amides: moderate, tendency to protonate Aromatic amides: strong	MS
Fragments		Amides: cleavage on both sides of the carbonyl group followed by loss of CO; large number of fragments of even mass Lactams: loss of α -substituent, loss of CO	
Rearrange- ments		Amides: elimination of the amine moiety, elimination of alkene from the amine or acid moiety in analogy to esters	
	$[M-18]^+$	Lactams	
$n \rightarrow \pi^*$	<220 nm (log ϵ 1–2)	Aliphatic amides and lactams	UV

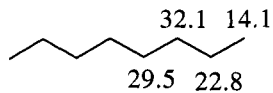
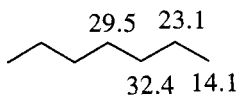
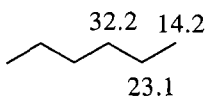
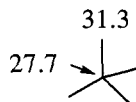
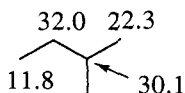
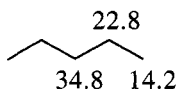
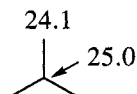
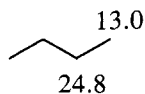
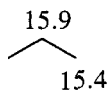
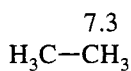
4 ^{13}C NMR Spectroscopy



4.1 Alkanes

4.1.1 Chemical Shifts

^{13}C Chemical Shifts of Alkanes (δ in ppm relative to TMS)



^{13}C Chemical Shifts of Methyl Groups (δ in ppm relative to TMS)

Substituent X	$\delta_{\text{CH}_3-\text{X}}$	Substituent X	$\delta_{\text{CH}_3-\text{X}}$		
C	-H	-2.3	-3-indolyl	9.8	
	-CH ₃	7.3	-4-indolyl	21.6	
	-CH ₂ CH ₃	15.4	-5-indolyl	21.5	
	-CH(CH ₃) ₂	24.1	-6-indolyl	21.7	
	-C(CH ₃) ₃	31.3	-7-indolyl	16.6	
	-(CH ₂) ₆ CH ₃	14.1	H a l	-F	71.6
	-CH ₂ -phenyl	15.7		-Cl	25.6
	-CH ₂ F	15.8		-Br	9.6
	-CH ₂ Cl	18.7		-I	-24.0
	-CH ₂ Br	19.1		O	-OH
	-CH ₂ I	20.4	-OCH ₃		60.9
	-CHCl ₂	31.6	-OCH ₂ CH ₃		57.6
	-CHBr ₂	31.8	-OCH(CH ₃) ₂		54.9
	-CCl ₃	46.3	-OC(CH ₃) ₃		49.4
	-CBr ₃	49.4	-OCH ₂ CH=CH ₂	57.4	
	-CH ₂ OH	18.2	-O-cyclohexyl	55.1	
	-CH ₂ OCH ₃	14.7	-OCH=CH ₂	52.5	
	-CH ₂ OCH ₂ CH ₃	15.4	-O-phenyl	54.8	
	-CH ₂ OCH=CH ₂	14.6	-OCOCH ₃	51.5	
	-CH ₂ O-phenyl	14.9	-OCO-cyclohexyl	51.2	
	-CH ₂ OCOCH ₃	14.4	-OCOCH=CH ₂	51.5	
	-CH ₂ NH ₂	19.0	-OCO-phenyl	51.8	
	-CH ₂ NHCH ₃	14.3	-OCOOCH ₃	54.9	
	-CH ₂ N(CH ₃) ₂	12.8	-OSO ₂ -4-tolyl	56.3	
	-CH ₂ NO ₂	12.3	-OSO ₂ OCH ₃	59.1	
	-CH ₂ SH	19.7	N	-NH ₂	28.3
	-CH ₂ SO ₂ CH ₃	6.7		-NH ₃ ⁺	26.5
	-CH ₂ SO ₃ H	8.0		-NHCH ₃	38.2
-CH ₂ CHO	5.2	-NH-cyclohexyl		33.5	
-CH ₂ COCH ₃	7.0	-NH-phenyl		30.2	
-CH ₂ COOH	9.6	-N(CH ₃) ₂		47.5	
-cyclopentyl	20.5	-N-pyrrolidinyl		42.7	
-cyclohexyl	23.1	-N-piperidinyl		47.7	
-CH=CH ₂	18.7	-N(CH ₃)phenyl		39.9	
-C \equiv CH	3.7	-N-pyrrolyl		35.9	
-phenyl	21.4	-N-imidazolyl		32.2	
-1-naphthyl	19.1	-N-pyrazolyl		38.4	
-2-naphthyl	21.5	-N-indolyl	32.1		
-2-pyridyl	24.2	-NHCOCH ₃	26.1		
-3-pyridyl	18.0	-N(CH ₃)CHO	31.5; 36.5		
-4-pyridyl	20.6	-N(CH ₃)COCH ₃	35.0; 38.0		
-2-furyl	13.7	-NO ₂	61.2		
-2-thienyl	14.7	-CN	1.7		
-2-pyrrolyl	11.8	-NC	26.8		
-2-indolyl	13.4	-NCS	29.1		

Substituent X	$\delta_{\text{CH}_3-\text{X}}$	Substituent X	$\delta_{\text{CH}_3-\text{X}}$
S -SH	6.5	-COO ⁻	24.4
-SCH ₃	19.3	-COOCH ₃	20.6
-S- <i>n</i> -C ₈ H ₁₇	15.5	-COOCOCH ₃	21.8
-S-phenyl	15.6	-CONH ₂	22.3
-SSCH ₃	22.0	-CON(CH ₃) ₂	21.5
-SOCH ₃	40.1	-COSH	32.6
-SO ₂ CH ₃	42.6	-COSCH ₃	30.2
-SO ₂ CH ₂ CH ₃	39.3	-COCOCH ₃	23.2
-SO ₂ Cl	52.6	-COCl	33.6
-SO ₃ H	39.6	-COBr	39.1
-SO ₃ Na	41.1	-COSi(CH ₃) ₃	35.7
O -CHO	31.2		
 -COCH ₃	30.7		
C -COCH ₂ CH ₃	27.5		
/\ -COCCl ₃	21.1		
-COCH=CH ₂	25.7		
-CO-cyclohexyl	27.6		
-CO-phenyl	25.7		
-COOH	21.7		



^{13}C Chemical Shifts of Monosubstituted Alkanes
(δ in ppm relative to TMS)

Substituent	Methyl -CH ₃	Ethyl		1-Propyl		
		-CH ₂	-CH ₃	-CH ₂	-CH ₂	-CH ₃
C						
-H	-2.3	7.3	7.3	15.4	15.9	15.4
-CH=CH ₂	18.7	27.4	13.4	36.2	22.4	13.6
-C \equiv CH	3.7	12.3	13.8	20.6	22.2	13.4
-phenyl	21.4	29.1	15.8	38.3	24.8	13.8
H						
-F	71.6	80.1	15.8	85.2	23.6	9.2
a						
-Cl	25.6	39.9	18.9	46.8	26.3	11.6
I						
-Br	9.6	27.6	19.4	35.6	26.4	13.0
-I	-24.0	-1.6	20.6	9.1	27.0	15.3
O						
-OH	50.2	57.8	18.2	64.2	25.9	10.3
-OCH ₃	60.9	67.7	14.7	74.5	23.2	10.5
-OCH ₂ CH ₃	57.6	66.0	15.4	72.5	23.2	10.7
-OCH(CH ₃) ₂	54.9					
-OC(CH ₃) ₃	49.4	56.8	16.4			
-O-phenyl	54.8	63.2	14.9	69.4	22.8	10.6
-OCOCH ₃	51.5	60.4	14.4	66.2	22.4	10.5
-OCO-phenyl	51.8	60.8	14.4	66.4	22.2	10.5
-OSO ₂ -4-tolyl	56.3	66.9	14.7	72.2	22.3	10.0
N						
-NH ₂	28.3	36.9	19.0	44.6	27.4	11.5
-NHCH ₃	38.2	45.9	14.3	54.0	23.2	12.5
-N(CH ₃) ₂	47.6	53.6	12.8	61.8	20.6	11.9
-NHCOCH ₃	26.1	34.4	14.6	40.7	22.5	11.1
-NO ₂	61.2	70.8	12.3	77.4	21.2	10.8
-CN	1.7	10.8	10.6	19.3	19.0	13.3
-NC	26.8	36.4	15.3	43.4	22.9	11.0
S						
-SH	6.5	19.1	19.7	26.4	27.6	12.6
-SCH ₃	19.3					
-SSCH ₃	22.0	31.8	14.7			
-SOCH ₃	40.1					
-SO ₂ CH ₃	42.6	48.2	6.7	56.3	16.3	13.0
-SO ₂ Cl	52.6	60.2	9.1	67.1	18.4	12.1
-SO ₂ OH	39.6	46.7	8.0	53.7	18.8	13.7
O						
-CHO	31.3	36.7	5.2	45.7	15.7	13.3
 						
-COCH ₃	30.7	35.2	7.0	45.2	17.5	13.5
C						
-CO-phenyl	25.7	31.7	8.3	40.4	17.7	13.8
/ \						
-COOH	21.7	28.5	9.6	36.2	18.7	13.7
-COOCH ₃	20.6	27.2	9.2	35.6	18.9	13.8
-CONH ₂	22.3	29.0	9.7			
-COCl	33.6	41.0	9.3	48.9	18.8	13.0

¹³C Chemical Shifts of Monosubstituted Alkanes (contd.)
 (δ in ppm relative to TMS)



Substituent	Isopropyl		<i>tert</i> -Butyl	
	-CH	-CH ₃	-C	-CH ₃
-H	15.9	15.4	25.0	24.1
C -CH=CH ₂	32.3	22.1	33.8	29.4
-C≡CH	20.3	22.8	27.4	31.1
-phenyl	34.3	24.0	34.6	31.4
H -F	87.3	22.6	93.5	28.3
a -Cl	53.7	27.3	66.7	34.6
l -Br	44.8	28.5	62.1	36.4
-I	20.9	31.2	43.0	40.4
-OH	64.0	25.3	68.9	31.2
-OCH ₃	72.6	21.4	72.7	27.0
-OCH ₂ CH ₃			72.6	27.7
-OCH(CH ₃) ₂	68.5	23.0	73.0	28.5
-OC(CH ₃) ₃	63.5	25.2	76.3	33.8
-O-phenyl	69.3	22.0		
-OCOCH ₃	67.5	21.9	79.9	28.1
-OCO-phenyl	68.2	21.9	80.7	28.2
N -NH ₂	43.0	26.5	47.2	32.9
-NHCH ₃	50.5	22.5	50.4	28.2
-N(CH ₃) ₂	55.5	18.7	53.6	25.4
-NHCOCH ₃	40.5	22.3	49.9	28.6
-NO ₂	78.8	20.8	85.2	26.9
-CN	19.8	19.9	28.1	28.5
-NC	45.5	23.4	54.0	30.7
S -SH	29.9	27.4	41.1	35.0
-SCH ₂ CH ₃	34.4	23.4		
-SO ₂ CH ₃	53.5	15.2	57.6	22.7
-SO ₂ Cl	67.6	17.1	74.2	24.5
-SO ₂ OH	52.9	16.8	55.9	25.0
O -CHO	41.1	15.5	42.4	23.4
 -COCH ₃	41.6	18.2	44.3	26.5
C -CO-phenyl	35.2	19.1	43.5	27.9
/ \ -COOH	34.1	18.8	38.7	27.1
-COOCH ₃	34.1	19.1	38.7	27.3
-CONH ₂	34.9	19.5	38.6	27.6
-COCl	46.5	19.0	49.4	27.1



^{13}C Chemical Shifts of 1-Substituted n-Octanes
(δ in ppm relative to TMS)

Substituent	1 -CH ₂	2 -CH ₂	3 -CH ₂	4 -CH ₂	5 -CH ₂	6 -CH ₂	7 -CH ₂	8 -CH ₃
-H	14.1	22.8	32.1	29.5	29.5	32.1	22.8	14.1
C -CH=CH ₂	34.5	~29.6	~29.6	~29.6	~29.6	32.2	23.0	13.9
-phenyl	36.2	31.7	~29.6	~29.6	~29.6	32.1	22.8	14.1
H -F	84.2	30.6	25.3	29.3	29.3	31.9	22.7	14.1
a -Cl	45.1	32.8	27.0	29.0	29.2	31.9	22.8	14.1
l -Br	33.8	33.0	28.3	28.8	29.2	31.8	22.7	14.1
-I	6.9	33.7	30.6	28.6	29.1	31.8	22.6	14.1
O -OH	63.1	32.9	25.9	29.5	29.4	31.9	22.8	14.1
-O-n-C ₈ H ₁₇	71.1	30.0	26.3	29.6	29.4	32.0	22.8	14.1
-ONO	68.3	29.2	26.0	29.3	29.3	31.9	22.7	14.0
N -NH ₂	42.4	34.1	27.0	29.6	29.4	31.9	22.7	14.1
-N(CH ₃) ₂	60.1	29.5*	~27.9*	~27.7*	29.7*	32.0	22.8	14.4
-NO ₂	75.8	26.2	27.9	~29.6	~29.6	31.4	22.6	14.0
-CN	17.2	25.5	~29.9	~29.9	~29.9	31.8	22.7	14.0
S -SH	24.7	34.2	28.5	29.2	29.1	31.9	22.7	14.1
-SCH ₃	34.5	29.0	29.4	29.4	29.4	31.9	22.8	14.1
-SO-n-C ₈ H ₁₇	52.6	~29.1	~29.1	~29.1	~29.1	31.8	22.7	14.1
O -CHO	44.0	22.2	~29.3	~29.3	~29.3	31.9	22.7	14.1
-COCH ₃	43.7	24.1	~29.5	~29.5	~29.5	32.0	22.8	14.1
C -CO-phenyl	38.6	24.4	29.5	29.5	29.5	31.9	22.7	14.0
/\ -COOH	34.2	24.8	~29.3	~29.3	~29.3	31.9	22.7	14.1
-COOCH ₃	34.2	25.1	29.3	29.3	29.3	31.9	22.8	14.1
-CONH ₂	35.5	25.4	29.1	29.1	29.1	31.6	22.3	14.0
-COCl	47.2	25.1	28.5	29.1	29.1	31.8	22.7	14.1

* assignment uncertain

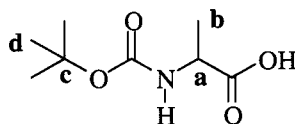
Estimation of ^{13}C Chemical Shifts of Aliphatic Compounds (in ppm relative to TMS)



The chemical shifts of sp^3 -hybridized carbon atoms can be estimated with the help of an additivity rule using the shift value of methane (-2.3 ppm) and increments for substituents in α -, β -, γ -, and δ -position (see next pages). Some substituents occupy two positions. Thus, the quaternary carbon atom **c** in the example given below is in δ -position relative to the carbon atom **a** since the sp^3 -hybridized oxygen of the β -COO group occupies the γ -position. This simple linear model needs corrections in case of strong branching of the observed C atom and/or its neighbors (steric corrections, S). Substituents for which such corrections are necessary are those with varying branching, i.e., a varying number of directly bonded H atoms. They are marked with an asterisk (*) in the Table of Increments. Further correction terms are needed if γ -substituents are in a sterically fixed position (conformational corrections, K).

The chemical shifts estimated with this additivity rule differ in general by less than about 4 ppm from the experimental values. Larger discrepancies may be expected for highly branched systems (particularly for quaternary carbon atoms). For carbon atoms bearing several halogen, oxygen, and/or other strongly deshielding substituents, additional correction terms are needed [1]. Without such corrections, deviations can be so large as to render the rule useless.

Example: Estimation of chemical shifts for *N*-tert-butoxycarbonylalanine



a	base value	-2.3
	1 α -C	9.1
	1 α -COOH	20.1
	1 α -NH	28.3
	1 β -COO	2.0
	1 δ -C	0.3
	1 S(tert,2)	-3.7
	estimated	53.8
	exp	49.0

b	base value	-2.3
	1 α -C	9.1
	1 β -COOH	2.0
	1 β -NH	11.3
	1 γ -COO	-2.8
	1 S(prim,3)	-1.1
	estimated	16.2
	exp	17.3

c	base value	-2.3
	3 α -C	27.3
	1 α -OCO	56.5
	1 γ -NH	-5.1
	1 δ -C	0.3
	3 S(quat,1)	-4.5
	estimated	72.2
	exp	78.1

d	base value	-2.3
	1 α -C	9.1
	2 β -C	18.8
	1 β -OCO	6.5
	1 δ -NH	0.0
	1 S(prim,4)	-3.4
	estimated	28.7
	exp	28.1



Estimation of ^{13}C Chemical Shifts of Aliphatic Compounds
(δ in ppm relative to TMS)

$$\delta = -2.3 + \sum_i Z_i + \sum_j S_j + \sum_k K_k$$

Substituent		Increment Z_i for substituents in position			
		α	β	γ	δ
	-H	0.0	0.0	0.0	0.0
	$-\text{C}\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} * \\ * \end{smallmatrix}$	9.1	9.4	-2.5	0.3
	$-\text{C}^*=\text{C}$	19.5	6.9	-2.1	0.4
	$-\text{C}\equiv\text{C}-$	4.4	5.6	-3.4	-0.6
	-phenyl	22.1	9.3	-2.6	0.3
H a l	-F	70.1	7.8	-6.8	0.0
	-Cl	31.0	10.0	-5.1	-0.5
	-Br	18.9	11.0	-3.8	-0.7
	-I	-7.2	10.9	-1.5	-0.9
O	$-\text{O}-^*$	49.0	10.1	-6.2	0.3
	$-\text{OCO}-$	56.5	6.5	-6.0	0.0
	$-\text{ONO}$	54.3	6.1	-6.5	-0.5
N	$-\text{N}\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} * \\ * \end{smallmatrix}$	28.3	11.3	-5.1	0.0
	$-\text{N}^+\begin{smallmatrix} \diagup \\ \diagdown \end{smallmatrix} \begin{smallmatrix} * \\ * \end{smallmatrix}$	30.7	5.4	-7.2	-1.4
	$-\text{NH}_3^+$	26.0	7.5	-4.6	0.0
	$-\text{NO}_2$	61.6	3.1	-4.6	-1.0
	$-\text{CN}$	3.1	2.4	-3.3	-0.5
	$-\text{NC}$	31.5	7.6	-3.0	0.0
S	$-\text{S}^*-$	10.6	11.4	-3.6	-0.4
	$-\text{SCO}-$	17.0	6.5	-3.1	0.0
	$-\text{S}^*\text{O}-$	31.1	7.0	-3.5	0.5
	$-\text{S}^*\text{O}_2-$	30.3	7.0	-3.7	0.3
	$-\text{SO}_2\text{Cl}$	54.5	3.4	-3.0	0.0
	$-\text{SCN}$	23.0	9.7	-3.0	0.0
O C	$-\text{CHO}$	29.9	-0.6	-2.7	0.0
	$-\text{CO}-$	22.5	3.0	-3.0	0.0
/ \	$-\text{COOH}$	20.1	2.0	-2.8	0.0
	$-\text{COO}^-$	24.5	3.5	-2.5	0.0
	$-\text{COO}-$	22.6	2.0	-2.8	0.0
	$-\text{CO}-\text{N}<$	22.0	2.6	-3.2	-0.4
	$-\text{COCl}$	33.1	2.3	-3.6	0.0
	$-\text{C}=\text{NOH syn}$	11.7	0.6	-1.8	0.0
	$-\text{C}=\text{NOH anti}$	16.1	4.3	-1.5	0.0
	$-\text{CS}-\text{N}<$	33.1	7.7	-2.5	0.6
	$-\text{Sn}$	-5.2	4.0	-0.3	0.0

Steric Corrections, *S*

Observed ^{13}C -center	S, for number of substituents at the α -atom ^a			
	1	2	3	4
primary (CH_3)	0.0	0.0	-1.1	-3.4
secondary (CH_2)	0.0	0.0	-2.5	-6.0
tertiary (CH)	0.0	-3.7	-8.5	-10.0
quaternary (C)	-1.5	-8.0	-10.0	-12.5

^a To be applied to each of the neighboring atoms, which may have a variable number of non-hydrogen substituents (marked with an asterisk (*) in the Table of Increments).

Conformational Corrections, *K*, for γ -Substituents

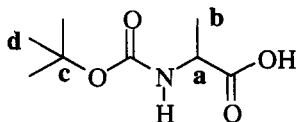
Conformation		K
synperiplanar		-4.0
synclinal		-1.0
anticlinal		0.0
antiperiplanar		2.0
not fixed		0.0

One can also use the chemical shifts of a reference compound as the base value if its structure is closely related to that assumed for the unknown. The increments corresponding to the structural elements missing in the reference compound are then added to the base value, while those of structural elements present in the reference but absent in the unknown are subtracted.

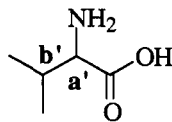


Example: Estimation of the chemical shifts for the carbon atoms **a** and **b** in *N*-*tert*-butoxycarbonylalanine using the chemical shifts of valine as base values (**a'**, **b'**):

Target:



Reference:



a	base value	61.6
	1 β -COO	2.0
	1 δ -C	0.3
	1 S(tert,2)	-3.7
	- 2 β -C	-18.8
	- 1 S(tert,3)	8.5
	estimated	49.9
	exp	49.0

b	base value	30.2
	1 γ -COO	-2.8
	1 S(prim,3)	-1.1
	- 2 α -C	-18.2
	- 1 S(tert,3)	8.5
	estimated	16.6
	exp	17.3

4.1.2

Coupling Constants

^{13}C - ^1H Coupling Constants

Coupling through one bond ($^1J_{\text{CH}}$ in Hz)

The ^{13}C - ^1H coupling constant of 125 Hz in methane increases in the presence of electronegative substituents and can be estimated by using the following additivity rule:

$$J_{\text{CH}} Z_1 Z_2 Z_3 = 125.0 + \sum_i Z_i$$

Substituent	Increments Z_i	Substituent	Increments Z_i
-H	0.0	-Br	27.0
-CH ₃	1.0	-I	26.0
-C(CH ₃) ₃	-3.0	-OH	18.0
-CH ₂ Cl	3.0	-O-phenyl	18.0
-CH ₂ Br	3.0	-NH ₂	8.0
-CH ₂ I	7.0	-NHCH ₃	7.0
-CHCl ₂	6.0	-N(CH ₃) ₂	6.0
-CCl ₃	9.0	-CN	11.0
-C \equiv C	7.0	-SOCH ₃	13.0
-phenyl	1.0	-CHO	2.0
-F	24.0	-COCH ₃	-1.0
-Cl	27.0	-COOH	5.5

Example: Estimation of ^{13}C - ^1H coupling constant of CHCl_3 :

$J = 125.0 + 3 \times 27.0 = 206.0$ Hz (exp: 209.0 Hz).

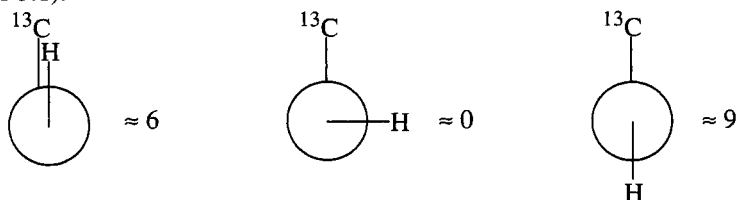
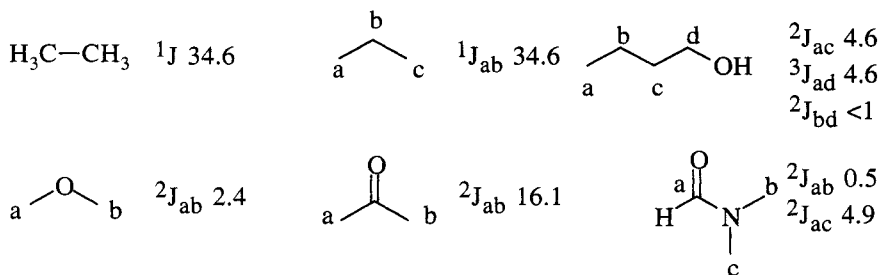
Coupling through more than one bond ($|J_{CH}|$ in Hz)

The coupling constants can be estimated from the corresponding ^1H - ^1H coupling constants [2]:

$$J_{CH} \approx 0.62 J_{HH}$$

$^2J_{CH}$	1–6	$^1\text{H}-\text{CH}_2-^{13}\text{CH}_3$	4.5
$^3J_{CH}$	0–10	$^1\text{H}-\text{CH}_2-\text{CH}_2-^{13}\text{CH}_3$	5.8

The ^{13}C - ^1H coupling constants for coupling across three bonds depend on the dihedral angle in the same way as the vicinal ^1H - ^1H coupling constants (see Chapter 5.1):

 **^{13}C - ^{13}C Coupling Constants ($|J_{CC}|$ in Hz)**

The ^{13}C - ^{13}C coupling constants for coupling over three bonds depend on the dihedral angle in the same way as the vicinal ^1H - ^1H (see Chapter 5.1) and ^{13}C - ^1H coupling constants. Maximum values of ca. 4–6 Hz are observed for dihedral angles of 0° and 180° and minimal values around 0 Hz at 90° .

4.1.3 References

- [1] A. Fürst, E. Pretsch, W. Robien, A comprehensive parameter set for the prediction of the ^{13}C NMR chemical shifts of sp^3 -hybridized carbon atoms in organic compounds, *Anal. Chim. Acta* **1990**, 233, 213.
- [2] J.L. Marshall, Carbon-carbon and carbon-proton NMR couplings, Verlag Chemie International, Deerfield Beach, FL, 1983.

4.2 Alkenes

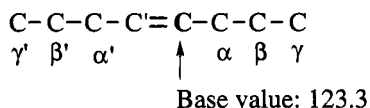
$\text{C}=\text{C}$ 4.2.1 Chemical Shifts

^{13}C Chemical Shifts of Alkenes (δ in ppm relative to TMS)

The ^{13}C chemical shifts of the carbons of $\text{C}=\text{C}$ double bonds typically range from ca. 80–160 ppm; a wider range of 40–210 ppm is observed with O- and N-substituents. In unsaturated *acyclic hydrocarbons*, they can be predicted with high accuracy (see below). To estimate the ^{13}C chemical shifts in all other *substituted alkenes*, one can use the substituent effects listed for chemical shifts in vinyl groups. However, since no configuration-dependent parameters are available, the values thus estimated are less accurate than those for unsaturated acyclic hydrocarbons.

The ^{13}C chemical shifts of sp^3 -hybridized carbon atoms in the vicinity of double bonds can be estimated using the additivity rule given on page 78. The conformational correction factors, K, for γ -substituents of *cis*- vs. *trans*-disubstituted alkenes differ by 6 ppm because the relative position of these substituents is fixed by the double bond.

Estimation of the ^{13}C Chemical Shifts of sp^2 -Hybridized Carbon Atoms in Unsaturated Acyclic Hydrocarbons (δ in ppm relative to TMS)



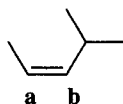
Increments for C-substituents:

at C-atom under consideration (C)		at neighboring C-atom (C')	
α	10.6	α'	-7.9
β	4.9	β'	-1.8
γ	-1.5	γ'	1.5

Steric corrections:

• for each pair of <i>cis</i> - α , α' -substituents	-1.1
• for a pair of geminal α , α -substituents	-4.8
• for a pair of geminal α' , α' -substituents	2.5
• if one or more β -substituents are present	2.3

Example: Estimation of chemical shifts of *cis*-4-methyl-2-pentene

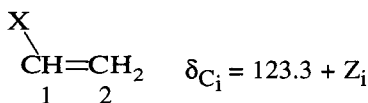


C=C

a	base value	123.3
	1 α -C	10.6
	1 α' -C	-7.9
	2 β' -C	-3.6
	<i>cis</i> - α, α'	-1.1
	estimated	121.3
	exp	121.8

b	base value	123.3
	1 α -C	10.6
	2 β -C	9.8
	1 α' -C	-7.9
	<i>cis</i> - α, α'	-1.1
	1 β -substituent	2.3
	estimated	137.0
	exp	138.8

Effect of Substituents on the ^{13}C Chemical Shifts of Vinyl Compounds (in ppm relative to TMS)



Substituent X	Z_1	Z_2	Substituent X	Z_1	Z_2
C -H	0.0	0.0	O -OH	25.7	-35.3
-CH ₃	12.9	-7.4	-OCH ₃	29.4	-38.9
-CH ₂ CH ₃	17.2	-9.8	-OCH ₂ CH ₃	28.8	-37.1
-CH ₂ CH ₂ CH ₃	15.7	-8.8	-O(CH ₂) ₃ CH ₃	28.1	-40.4
-CH(CH ₃) ₂	22.7	-12.0	-OCOCH ₃	18.4	-26.7
-(CH ₂) ₃	14.6	-8.9	N -N(CH ₃) ₂	28.0*	-32.0*
-C(CH ₃) ₃	26.0	-14.8	-N ⁺ (CH ₃) ₃	19.8	-10.6
-CH ₂ Cl	10.2	-6.0	-N-pyrrolidonyl	6.5	-29.2
-CH ₂ Br	10.9	-4.5	-NO ₂	22.3	-0.9
-CH ₂ I	14.2	-4.0	-CN	-15.1	14.2
-CH ₂ OH	14.2	-8.4	-NC	-3.9	-2.7
-CH ₂ OCH ₂ CH ₃	12.3	-8.8	S -SCH ₂ CH ₃	9.0	-12.8
-CH=CH ₂	13.6	-7.0	-SO ₂ CH=CH ₂	14.3	7.9
-C≡CH	-6.0	5.9	O -CHO	15.3	14.5
-phenyl	12.5	-11.0	 -COCH ₃	13.8	4.7
H -F	24.9	-34.3	C -COOH	5.0	9.8
-Cl	2.8	-6.1	/\ -COOCH ₂ CH ₃	6.3	7.0
-Br	-8.6	-0.9	-COCl	8.1	14.0
-I	-38.1	7.0	-Si(CH ₃) ₃	16.9	6.7
			-SiCl ₃	8.7	16.1

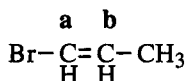
* estimated values

The values listed on the preceding page can also be used to estimate the ^{13}C chemical shifts of sp^2 -hybridized carbon atoms in alkenes with more than one substituent (note that the *cis/trans* configuration is not taken into account):

$$\delta_{\text{C}_i} = 123.3 + \sum_i Z_i$$

C = C

Example: Estimation of chemical shifts of 1-bromo-1-propene



a	base value	123.3		b	base value	123.3
	$Z_1(\text{Br})$	-8.6			$Z_2(\text{Br})$	-0.9
	$Z_2(\text{CH}_3)$	-7.4			$Z_1(\text{CH}_3)$	12.9
	estimated	107.3			estimated	135.3
	exp	108.9	(<i>cis</i>)		exp	129.4
		104.7	(<i>trans</i>)			132.7
						(<i>trans</i>)

The following examples show some larger deviations between measured and estimated (in parentheses) chemical shifts. This is usually to be expected when several substituents are present that strongly interact with the π -electrons of the double bond:

$\text{NC} \begin{array}{c} \text{a} \quad \text{b} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{NC} \quad \text{N}(\text{CH}_3)_2 \end{array}$	a	39.1 (29.1)	$\text{H} \begin{array}{c} \text{a} \quad \text{b} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{N}(\text{CH}_3)_2 \end{array}$	a	69.2 (59.3)
	b	171.0 (207.7)		b	163.0 (179.3)
$\text{H} \begin{array}{c} \text{a} \quad \text{b} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ (\text{H}_3\text{C})_2\text{N} \quad \text{NO}_2 \end{array}$	a	151.0 (150.4)	$\text{H} \begin{array}{c} \text{a} \quad \text{b} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{OCH}_3 \end{array}$	a	54.7 (45.5)
	b	111.4 (113.6)		b	167.9 (182.1)

^{13}C Chemical Shifts of *cis*- and *trans*-1,2-Disubstituted Alkenes
(δ in ppm relative to TMS)

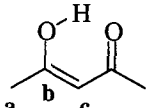
Substituent R	$\begin{array}{c} \text{R} \quad \text{R} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{H} \end{array}$	$\begin{array}{c} \text{R} \quad \text{H} \\ \diagdown \quad \diagup \\ \text{C}=\text{C} \\ \diagup \quad \diagdown \\ \text{H} \quad \text{R} \end{array}$
$-\text{CH}_3$	123.3	124.5
$-\text{CH}_2\text{CH}_3$	131.2	131.3
$-\text{Cl}$	118.1	119.9
$-\text{Br}$	116.4	109.4
$-\text{I}$	96.5	79.4
$-\text{CN}$	120.8	120.2
$-\text{OCH}_3$	130.3	135.2
$-\text{COOH}$	130.4	134.2
$-\text{COOCH}_3$	130.1	133.5

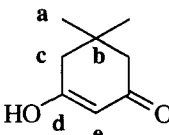
¹³C Chemical Shifts of Enols (δ in ppm relative to TMS)

The carbon atom bonded to the enolic OH group is strongly deshielded so that its shift is close to that of a carbonyl carbon. The other carbon atom is strongly shielded.

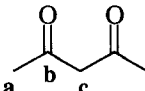
C=C

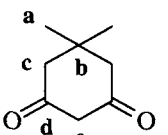
Enol:

	a	22.5
	b	190.5
	c	99.0

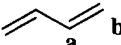
	a	28.3
	b	32.8
	c	46.2
	d	191.1
	e	103.3

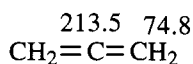
Ketone:

	a	28.5
	b	201.1
	c	56.6

	a	28.3
	b	31.0
	c	54.2
	d	203.6
	e	57.3

¹³C Chemical Shifts of Aliphatic Dienes (δ in ppm relative to TMS)***Conjugated Dienes***

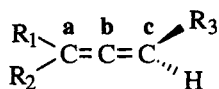
	a	136.9
	b	116.3

Allenes

Estimation of the chemical shifts of sp^2 -hybridized carbon atoms in substituted allenes: see [1].

^{13}C Chemical Shifts of Substituted Allenes
(δ in ppm relative to TMS)

$\text{C}=\text{C}$



R_1	R_2	R_3	a	b	c
-H	-H	-H	74.8	213.5	74.8
-CH ₃	-H	-H	84.4	210.4	74.1
-CH ₃	-CH ₃	-H	93.4	207.3	72.1
-CH ₃	-H	-CH ₃	85.4	207.1	85.4
-CH ₂ CH ₃	-H	-H	91.7	208.9	75.3
-C(CH ₃) ₃	-C(CH ₃) ₃	-H	119.6	207.0	75.8
-CH=CH ₂	-H	-H	93.9	211.4	75.1
-C \equiv CH	-H	-H	74.8	217.7	77.3
-phenyl	-H	-H	94.4	210.0	78.8
-F	-H	-H	129.8	200.2	93.9
-Cl	-H	-H	88.8	207.9	84.5
-Br	-H	-H	72.7	207.6	83.8
-I	-H	-H	35.3	208.0	78.3
-OCH ₃	-H	-H	123.1	202.0	90.3
-N(CH ₃) ₂	-H	-H	113.1	204.2	85.5
-CN	-H	-H	67.4	218.7	80.7
-SCH ₃	-H	-H	90.0	206.1	81.3
-COOH	-H	-H	88.1	217.7	80.0

4.2.2
Coupling Constants

^{13}C - ^1H Coupling Constants ($|J_{\text{CH}}|$ in Hz)

Coupling through one bond



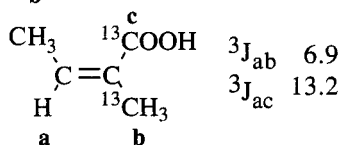
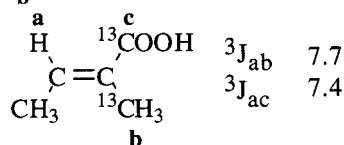
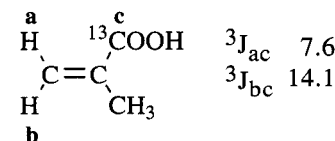
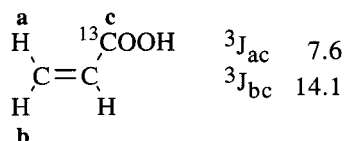
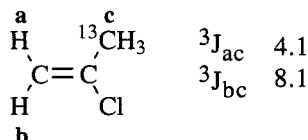
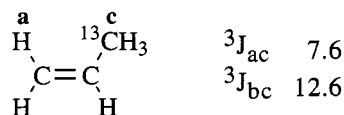
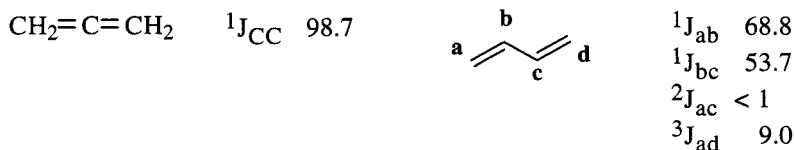
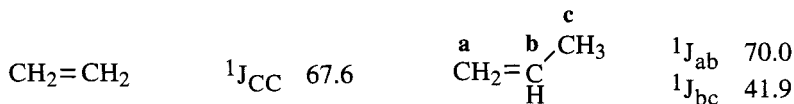
Coupling through two bonds (typical range: 0–16)



Additivity rule for the estimation of ${}^2J_{\text{CH}}$ of alkenes: see [2].

Coupling through three bonds:

The *trans*- $^1\text{H}-\text{C}=\text{C}-^{13}\text{C}$ coupling constant of alkenes is always larger than the corresponding *cis* coupling constant so that an assignment is possible if both isomers are available: see [3].

C=C **^{13}C - ^{13}C Coupling Constants ($|^1J_{CC}|$ in Hz)****4.2.3
References**

- [1] R.H.A.M. Janssen, R.J.J.Ch. Lousberg, M.J.A. de Bie, An additivity relation for carbon-13 chemical shifts in substituted allenes, *J. R. Neth. Chem. Soc.* **1981**, 100, 85.
- [2] U. Vögeli, D. Herz, W. von Philipsborn, Geminal C,H spin coupling in substituted alkenes, *Org. Magn. Reson.* **1980**, 13, 200.
- [3] U. Vögeli, W. von Philipsborn, Vicinal C,H spin coupling in substituted alkenes. Stereochemical significance and structural effects, *Org. Magn. Reson.* **1975**, 7, 617.

4.3 Alkynes

4.3.1 Chemical Shifts

$\text{C}\equiv\text{C}$ ^{13}C Chemical Shifts of Alkynes (δ in ppm relative to TMS)

		a	b
		$\text{X}-\text{C}\equiv\text{C}-\text{H}$	
Substituent X		a	b
	-H	71.9	71.9
C	-CH ₃	80.4	68.3
	-CH ₂ CH ₃	85.5	67.1
	-CH ₂ CH ₂ CH ₃	84.0	68.7
	-CH ₂ CH ₂ CH ₂ CH ₃	83.0	66.0
	-CH(CH ₃) ₂	89.2	67.6
	-C(CH ₃) ₃	92.6	66.8
	-cyclohexyl	88.7	68.3
	-CH ₂ OH	83.0	73.8
	-CH=CH ₂	82.8	80.0
	-C \equiv C-CH ₃	68.8	64.7
	-phenyl	84.6	78.3
O	-OCH ₂ CH ₃	90.9	26.5
S	-SCH ₂ CH ₃	72.6	81.4
O	-CHO	81.8	83.1
	-COCH ₃	81.9	78.1
C	-COOH	74.0	78.6
/\	-COOCH ₃	74.8	75.6

Additivity rule for estimating the chemical shifts of *sp*-hybridized carbon atoms in alkynes: see [1].

4.3.2 Coupling Constants

¹³C-¹H Coupling Constants ($|J_{CH}|$ in Hz) [2]

^a	^b	^c	¹ J _{ab}	249	
H— ¹³ C≡C—H			² J _{bc}	49.3 (in substituted acetylenes: 40–60)	

^a	^b	^c	^{d e}	² J _{ac}	50.1	³ J _{ad}	3.4	
H—C≡C—CH ₃				² J _{ce}	-10.4	³ J _{be}	4.7	C≡C

^a	^b	^c	² J _{ab}	-10.3	³ J _{ac}	4.3	
CH ₃ —C≡C—CH ₃							

With acetylenes, the results of multipulse experiments (such as DEPT, INEPT, SEFT, or APT) to determine the number of protons attached to the carbon atoms must be interpreted with care. As a consequence of the unusually large ¹³C-¹H coupling constants through one and two bonds, the sign of the signals may be opposite to the expected one.

¹³C-¹³C Coupling Constants ($|J_{CC}|$ in Hz)

		^a	^b	^c	¹ J _{ab}	190.3
H—C≡C—H	¹ J _{CC}	171.5	H—C≡C—C≡C—H		¹ J _{bc}	153.4









4.3.3 References

- [1] W. Höbold, R. Radechia, D. Klose, Inkrementen-Berechnung von ¹³C-chemischen Verschiebungen in *n*-Alkinen, J. Prakt. Chem. **1976**, 318, 519.
- [2] K. Hayamizu, O. Yamamoto, ¹³C, ¹H Spin coupling constants of dimethylacetylene, Org. Magn. Reson. **1980**, 13, 460.

4.4 Alicyclics

4.4.1 Chemical Shifts

Saturated Monocyclic Alicyclics (δ in ppm relative to TMS)

		-2.8		27.1		$(\text{CH}_2)_n$		
		22.9		28.8				
		25.6		26.8				

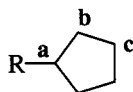
n	δ
9	26.0
10	25.1
11	26.3
12	23.8
13	26.2
14	25.2
15	27.0
20	28.0
30	29.3
40	29.4
72	29.7

^{13}C Chemical Shifts of Monosubstituted Cyclopropanes
(δ in ppm relative to TMS) [1]



Substituent X	a	b	other
-H	-2.8	-2.8	
C -CH ₃	4.9	5.6	CH ₃ 19.4
-CH ₂ CH ₃	12.8	4.1	CH ₂ 27.8, CH ₃ 13.6
-CH ₂ CH ₂ CH ₂ CH ₃	10.9	4.4	1-CH ₂ 34.7, 2-CH ₂ 32.0
-C(CH ₃) ₃	22.7	0.3	C 29.3, CH ₃ 28.2
-CH ₂ Cl	13.6	5.5	CH ₂ 50.3
-CH ₂ OH	12.7	2.2	CH ₂ 66.5
-CH=CH ₂	14.7	6.6	CH 142.4, CH ₂ 111.5
-phenyl	15.3	9.2	C 143.9, CH 125.3–128.2
H -Cl	27.3	8.9	
a -Br	14.2	9.1	
I -I	-20.1	10.4	
O -OH	45.7	6.8	
N -NH ₂	24.0	7.4	
-NO ₂	54.3	11.7	
-CN	-4.5	6.2	CN 121.5
O -CHO	22.7	7.4	CO 202.1
 -COCH ₃	20.1	9.6	CO 207.3, CH ₃ 29.1
C -COOH	12.7	8.9	CO 181.6
/\ -COOCH ₃	12.2	7.7	CO 174.7, CH ₃ 51.1

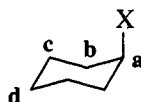
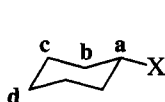
¹³C Chemical Shifts of Monosubstituted Cyclopentanes
(δ in ppm relative to TMS) [2]




Substituent X	a	b	c	other
-H	25.5	25.5	25.5	
C -CH ₃	34.8	34.8	25.4	CH ₃ 21.4
-CH ₂ CH ₃	42.3	32.6	25.4	CH ₂ 29.2, CH ₃ 13.2
-CH(CH ₃) ₂	47.4	30.0	24.7	CH 33.9, CH ₃ 21.7
-C(CH ₃) ₃	50.3	26.5	25.1	C 32.5, CH ₃ 27.6
-CH ₂ OH	41.2	28.3	24.5	CH ₂ 67.0
H -F	95.5	32.8	22.5	¹ J _{CF} 173.5, ² J _{CF} 22.1, ³ J _{CF} <1.5
a -Cl	61.8	37.5	23.3	
I -Br	53.1	38.4	23.7	
-I	28.7	40.7	24.9	
O -OH	72.5	34.5	22.7	
-OCH ₃	82.2	31.4	23.1	CH ₃ 56.0
-OCOCH ₃	77.7	33.8	24.9	CO 170.8, CH ₃ 21.7
N -NH ₂	52.5	35.5	23.0	
-NO ₂	87.0	32.6	24.8	
-CN	27.0	30.5	24.2	CN 123.4
S -SH	38.3	37.7	24.6	
-COOH	43.0	29.2	25.1	CO 183.8



^{13}C Chemical Shifts of Equatorially and Axially Monosubstituted Cyclohexanes (δ in ppm relative to TMS)

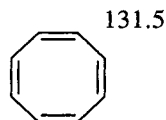
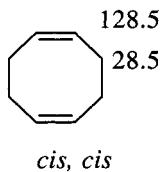
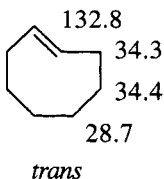
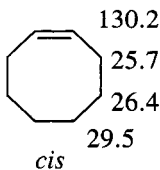
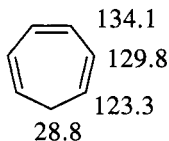
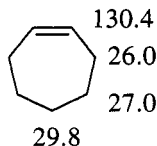
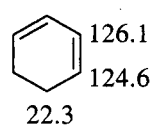
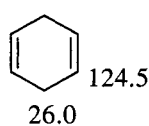
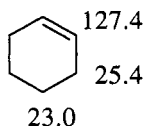
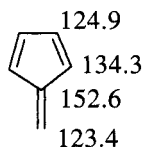
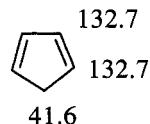
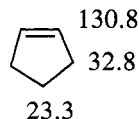
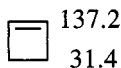
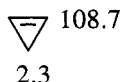


Substituent X	a	b	c	d	a	b	c	d
 -H	27.1	27.1	27.1	27.1	27.1	27.1	27.1	27.1
C -CH ₃	33.2	36.0	27.1	27.0	28.4	32.4	20.6	26.9
-CH ₂ CH ₃	40.1	33.4	26.9	27.2	35.5	30.0	21.4	27.1
-CH ₂ CH ₂ CH ₃	40.0	33.6	26.6	26.9				
-CH(CH ₃) ₂	44.6	30.0	26.8	27.3	41.1	30.2	21.6	27.1
-CH ₂ CH ₂ CH ₂ CH ₃	38.4	34.1	27.1	27.3				
-C(CH ₃) ₃	48.8	28.1	27.7	27.1				
-cyclohexyl	44.3	30.8	27.4	27.4				
-CH=CH ₂	42.1	32.3	26.0	27.1	37.0	30.0	21.2	27.1
-C≡CH	28.7	32.1	25.2	24.4	28.0	30.0	21.2	25.7
-phenyl	45.1	34.9	27.4	26.7				
H -F	91.0	32.8	23.6	25.3	88.1	30.1	19.8	25.0
a -Cl	59.8	37.4	26.1	25.4	60.1	33.9	20.4	26.0
i -Br	52.4	38.3	27.3	25.6	55.4	34.9	21.5	26.4
-I	31.2	40.1	28.3	25.4	38.3	36.0	22.8	26.1
O -OH	70.4	35.8	25.1	26.3	65.5	33.2	20.5	27.1
-OCH ₃	79.2	32.2	24.5	26.4	74.9	30.0	21.1	26.6
-OCOCH ₃	72.3	32.2	24.4	26.1				
-OCO-phenyl	72.8	31.5	24.1	24.7	69.0	29.3	20.3	24.7
-OSi(CH ₃) ₃	70.5	36.0	24.7	25.0	66.1	33.1	19.8	25.0
N -NH ₂	51.1	37.6	25.8	26.3	47.4	33.8	20.0	27.1
-NHCH ₃	58.7	32.7	25.7	26.8				
-N(CH ₃) ₂	64.3	29.2	26.5	26.9				
-NH ₃ ⁺ Cl ⁻	51.8	32.2	24.8	25.2				
-N=C=N-cyclohexyl	55.7	35.0	24.8	25.5				
-NO ₂	84.6	31.4	24.7	25.5				
-N ₃	59.5	31.5	24.5	24.5	56.8	29.0	20.1	25.2
-CN	28.0	29.6	24.6	25.1	26.4	27.4	21.9	25.0
-NC	51.9	33.7	24.4	25.2	50.3	30.5	20.1	25.2
-NCS	55.3	33.9	24.5	24.8	50.3	30.5	20.1	25.2
S -SH	38.3	38.1	26.6	25.3	35.9	33.1	19.4	25.7
O -CHO	50.1	26.0	25.2	26.1	46.4	24.7	22.7	27.1
 -COCH ₃	51.5	29.0	26.6	26.3				
C -COOH	43.7	29.6	26.2	26.6				
/\ -COO ⁻	47.2	30.9	26.9	26.9				
-COOCH ₃	43.4	29.6	26.0	26.4	39.1	27.7	24.1	26.7
-COCl	55.4	29.7	25.5	25.9				

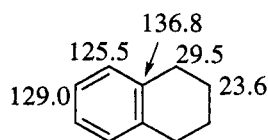
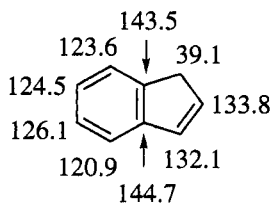
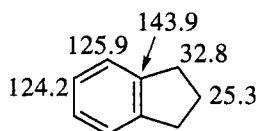
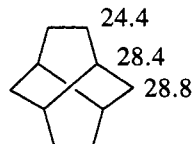
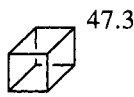
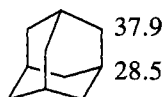
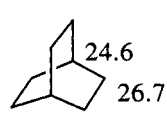
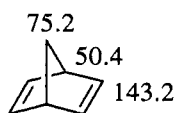
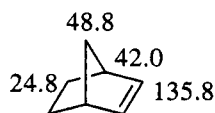
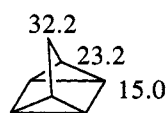
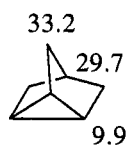
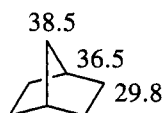
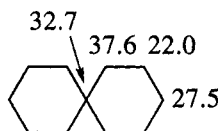
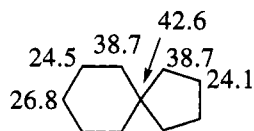
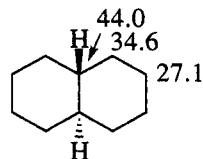
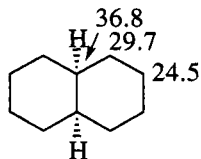
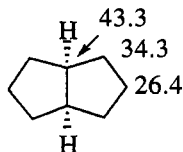
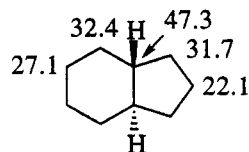
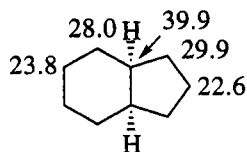
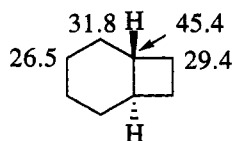
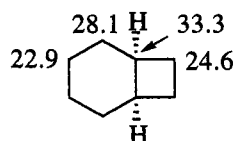
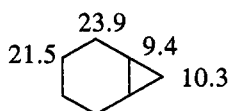
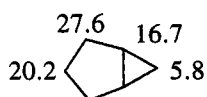
Estimation of ^{13}C Chemical Shifts of Alicyclic Compounds
(in ppm relative to TMS)

The chemical shift of the parent compound (e.g., 22.9 for cyclobutane, 25.6 for cyclopentane, and 27.1 ppm for cyclohexane) and the same increments as for alkanes (see Chapter 4.1) can be used to estimate the chemical shifts of sp^3 -hybridized carbon atoms of alicyclic compounds. Appropriate use of the conformational correction terms, K (page 79), is especially important with axial and equatorial substituents in cyclohexanes. The additivity rule is, however, not suitable for estimating chemical shifts of substituted cyclopropanes.

^{13}C Chemical Shifts of Unsaturated Alicyclics
(δ in ppm relative to TMS)



^{13}C Chemical Shifts of Condensed Alicyclics
 (δ in ppm relative to TMS)



4.4.2 Coupling Constants

^{13}C - ^1H Coupling Constants

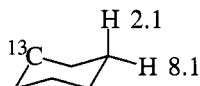
Coupling through one bond ($|^1J_{\text{CH}}|$ in Hz)



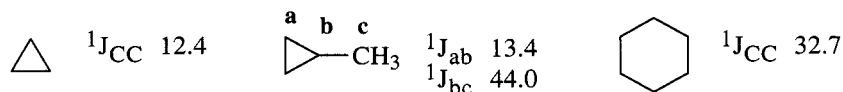
Coupling through two bonds ($|^2J_{\text{CH}}|$ in Hz)



Coupling through three bonds ($|^3J_{\text{CH}}|$ in Hz)



^{13}C - ^{13}C Coupling Constants ($|^1J_{\text{CC}}|$ in Hz)



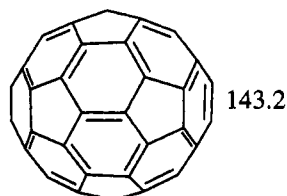
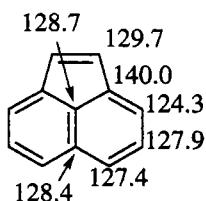
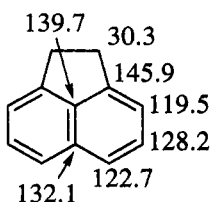
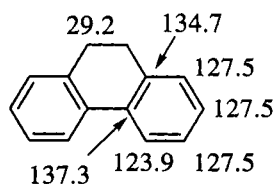
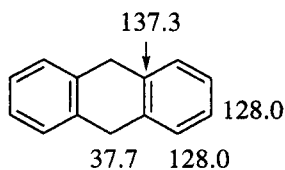
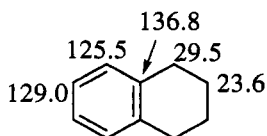
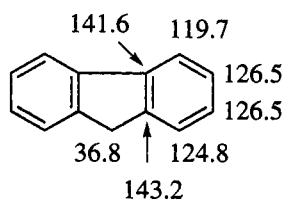
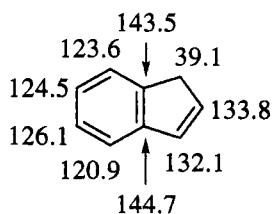
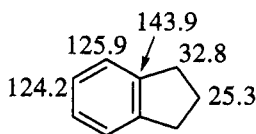
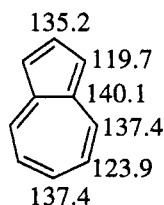
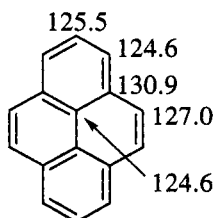
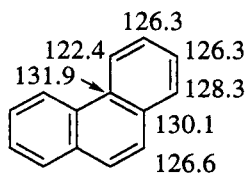
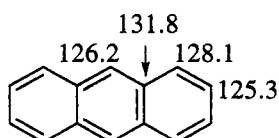
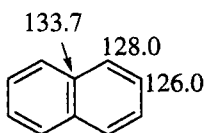
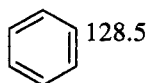
4.4.3 References

- [1] N.C. Rol, A.D.H. Clague, ^{13}C NMR Spectroscopy of cyclopropane derivatives, *Org. Magn. Reson.* **1981**, 16, 187.
- [2] H.-J. Schneider, N. Nguyen-Ba, F. Thomas, Force field and ^{13}C NMR investigations of substituted cyclopentanes. A concept for the adaption of ^{13}C NMR shifts to varying torsional arrangements in flexible conformers, *Tetrahedron* **1982**, 38, 2327.

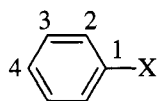
4.5 Aromatic Hydrocarbons

4.5.1 Chemical Shifts

^{13}C Chemical Shifts in Aromatic Hydrocarbons
(δ in ppm relative to TMS) [1]



Effect of Substituents on ^{13}C Chemical Shifts of Monosubstituted Benzenes (in ppm relative to TMS)



$$\delta_{\text{C}_i} = 128.5 + Z_i$$

Substituent X	Z_1	Z_2	Z_3	Z_4
C -H	0.0	0.0	0.0	0.0
-CH ₃	9.2	0.7	-0.1	-3.0
-CH ₂ CH ₃	11.7	-0.6	-0.1	-2.8
-CH ₂ CH ₂ CH ₃	10.3	-0.2	0.1	-2.7
-CH(CH ₃) ₂	20.2	-2.2	-0.3	-2.8
-CH ₂ CH ₂ CH ₂ CH ₃	10.9	-0.2	-0.2	-2.8
-C(CH ₃) ₃	18.6	-3.3	-0.4	-3.1
-cyclopropyl	15.1	-3.3	-0.6	-3.6
-cyclopentyl	17.8	-1.5	-0.4	-2.9
-cyclohexyl	16.3	-1.8	-0.3	-2.8
-1-adamantyl	22.2	-2.9	-0.5	-3.1
-CH ₂ F	8.5	-0.7	0.4	0.5
-CF ₃	2.5	-3.2	0.3	3.3
-CH ₂ Cl	9.3	0.3	0.2	0.0
-CHCl ₂	11.9	-2.4	0.1	1.2
-CCl ₃	16.3	-1.7	-0.1	1.8
-CH ₂ Br	9.5	0.7	0.3	0.2
-CH ₂ I	10.5	0.0	0.0	-0.9
-CH ₂ OH	12.4	-1.2	0.2	-1.1
-CH ₂ OCH ₃	8.7	-0.9	-0.1	-0.9
-CH ₂ NH ₂	14.9	-1.4	-0.2	-2.0
-CH ₂ NHCH ₃	12.6	-0.3	-0.3	-1.8
-CH ₂ N(CH ₃) ₂	7.8	0.5	-0.3	-1.5
-CH ₂ NO ₂	2.2	2.2	2.2	1.2
-CH ₂ CN	1.6	0.5	-0.8	-0.7
-CH ₂ SH	12.5	-0.6	0.0	-1.6
-CH ₂ SCH ₃	9.8	0.4	-0.1	-1.6
-CH ₂ S(O)CH ₃	0.8	1.5	0.4	-0.2
-CH ₂ SO ₂ CH ₃	-0.1	2.1	0.6	0.6
-CH ₂ CHO	7.4	1.3	0.5	-1.1
-CH ₂ COCH ₃	5.8	0.8	0.1	-1.6
-CH ₂ COOH	6.5	1.4	0.4	-1.2
-CH ₂ Li	32.2	-22.0	-0.4	-24.3
-CH=CH ₂	8.9	-2.3	-0.1	-0.8
-C(CH ₃)=CH ₂	12.6	-3.1	-0.4	-1.2
-C≡CH	-6.2	3.6	-0.4	-0.3
-phenyl	8.1	-1.1	0.5	-1.1
-2-pyridyl	11.2	-1.4	0.5	-1.4
-4-pyridyl	9.6	-1.6	0.5	0.5



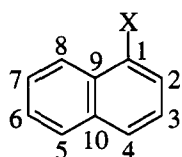


	Substituent X	Z ₁	Z ₂	Z ₃	Z ₄
H a l	-F	33.6	-13.0	1.6	-4.4
	-Cl	5.3	0.4	1.4	-1.9
	-Br	-5.4	3.3	2.2	-1.0
	-I	-31.2	8.9	1.6	-1.1
O	-OH	28.8	-12.8	1.4	-7.4
	-ONa	39.6	-8.2	1.9	-13.6
	-OCH ₃	33.5	-14.4	1.0	-7.7
	-OCH=CH ₂	28.2	-11.5	0.7	-5.8
	-O-phenyl	27.6	-11.2	-0.3	-6.9
	-OCOCH ₃	22.4	-7.1	0.4	-3.2
	-OSi(CH ₃) ₃	26.8	-8.4	0.9	-7.1
	-OPO(O-phenyl) ₂	21.9	-8.4	1.2	-3.0
	-OCN	25.0	-12.7	2.6	-1.0
N	-NH ₂	18.2	-13.4	0.8	-10.0
	-NHCH ₃	15.0	-16.2	0.8	-11.6
	-N(CH ₃) ₂	16.0	-15.4	0.9	-10.5
	-NH-phenyl	14.7	-10.6	0.9	-10.5
	-N(phenyl) ₂	13.1	-7.0	0.9	-5.6
	-NH ₃ ⁺	0.1	-5.8	2.2	2.2
	-NH ₂ ⁺ CH(CH ₃) ₂	5.5	-4.1	1.1	0.7
	-N ⁺ (CH ₃) ₃	19.5	-7.3	2.5	2.4
	-N(O)(CH ₃) ₂	26.2	-8.4	0.8	0.6
	-NHCOCH ₃	9.7	-8.1	0.2	-4.4
	-NHOH	21.5	-13.1	-2.2	-5.3
	-NHNH ₂	22.8	-16.5	0.5	-9.6
	-N(NO)CH ₃	13.7	-9.4	0.9	-1.3
	-N=CH-phenyl	24.7	-6.5	1.3	-1.5
	-N=NCH ₃	22.2	-6.2	0.5	-3.0
	-NO	37.4	-7.6	0.8	7.1
	-NO ₂	19.9	-4.9	0.9	6.1
	-CN	-16.0	3.5	0.7	4.3
	-NC	-1.8	-2.2	1.4	0.9
	-NCO	5.1	-3.7	1.1	-2.8
	-NCS	3.0	-2.7	1.3	-1.0
	-N ⁺ ≡N	-12.7	6.0	5.7	16.0
S	-SH	4.0	0.7	0.3	-3.2
	-SCH ₃	10.0	-1.9	0.2	-3.6
	-SC(CH ₃) ₃	4.5	9.0	-0.3	0.0
	-S(CH ₃) ₂ ⁺	-1.0	3.1	2.2	6.3
	-SCH=CH ₂	5.8	2.0	0.2	-1.8
	-S-phenyl	7.3	2.5	0.6	-1.5
	-S-S-phenyl	7.5	-1.3	0.8	-1.1
	-S(O)CH ₃	17.6	-5.0	1.1	2.4
	-SO ₂ CH ₃	12.3	-1.4	0.8	5.1
	-SO ₂ OH	15.0	-2.2	1.3	3.8
	-SO ₂ OCH ₃	6.4	-0.6	1.5	5.9
	-SO ₂ F	4.6	0.0	1.5	7.5

	Substituent X	Z ₁	Z ₂	Z ₃	Z ₄
O C /\	-SO ₂ Cl	15.6	-1.7	1.2	6.8
	-SO ₂ NH ₂	10.8	-3.0	0.3	3.2
	-SCN	-3.7	2.5	2.2	2.2
	-CHO	8.2	1.2	0.5	5.8
	-COCH ₃	8.9	0.1	-0.1	4.4
	-COCF ₃	-5.6	1.8	0.7	6.7
	-COC≡CH	7.4	1.0	0.0	5.9
	-CO-phenyl	9.3	1.6	-0.3	3.7
	-COOH	2.1	1.6	-0.1	5.2
	-COONa	9.7	4.6	2.2	4.6
	-COOCH ₃	2.0	1.2	-0.1	4.3
	-CONH ₂	5.0	-1.2	0.1	3.4
	-CON(CH ₃) ₂	6.0	-1.5	-0.2	1.0
	-COF	4.2	1.6	-0.7	5.3
	-COCl	4.7	2.7	0.3	6.6
	-COSH	6.2	-0.6	0.2	5.4
	-CH=NCH ₃	8.8	0.5	0.1	2.3
	-CS-phenyl	18.7	1.0	-0.6	2.4
	-CS-(1-piperidyl)	15.0	-3.1	-0.2	-0.2
	-Li	-43.2	-12.7	2.4	3.1
	-MgBr	-35.8	-11.4	2.7	4.0
Si	-SiH ₃	-0.5	7.3	-0.4	1.3
	-SiH ₂ CH ₃	4.8	6.3	-0.5	1.0
	-Si(CH ₃) ₃	11.6	4.9	-0.7	0.4
	-Si(phenyl) ₃	5.8	7.9	-0.6	1.1
	-SiCl ₃	3.0	4.6	0.1	4.2
	-Ge(CH ₃) ₃	13.7	4.5	-0.5	-0.2
	-Sn(CH ₃) ₃	13.2	7.2	-0.4	-0.4
P	-Pb(CH ₃) ₃	20.1	8.0	-0.1	-1.0
	-P(CH ₃) ₂	13.6	1.6	-0.6	-1.0
	-P(phenyl) ₂	8.9	5.2	0.0	0.1
	-P ⁺ (phenyl) ₂ CH ₃	-9.7	5.2	2.0	6.7
	-PO(CH ₃) ₂	2.5	1.1	0.1	3.0
	-PO(-phenyl) ₂	5.8	3.9	-0.1	3.0
	-PO(OH) ₂	-1.9	3.6	1.5	5.6
	-PO(OCH ₂ CH ₃) ₂	1.6	3.6	-0.2	3.4
	-PS(CH ₃) ₂	6.7	2.0	0.2	2.9
	-PS(OCH ₂ CH ₃) ₂	6.1	2.8	-0.4	3.4
	-AsH ₂	1.7	7.9	0.8	0.0
	-As(phenyl) ₂	11.1	5.0	0.1	-0.1
	-AsO(OH) ₂	3.8	1.6	0.8	4.5
	-SeCH=CH ₂	0.7	4.7	0.4	-1.4
	-SeCN	-5.3	5.1	2.9	2.1
	-Sb(phenyl) ₂	9.8	7.7	0.3	0.0
	-Hg-phenyl	41.6	9.3	-0.9	-1.6
	-HgCl	22.5	8.0	-0.6	-0.9



Effect of Substituents in Position 1 on the ^{13}C Chemical Shifts of Monosubstituted Naphthalenes (in ppm relative to TMS)



for X: H $\delta_{\text{C}_1} = 128.0$

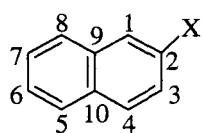
$\delta_{\text{C}_2} = 125.9$

$\delta_{\text{C}_9} = 133.6$

Substituent X	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
C -CH ₃	6.0	0.5	0.6	-1.8	0.3	-0.7	-0.5	-4.1	-1.1	-0.2
-C(CH ₃) ₃	17.9	-2.8	-0.9	-0.6	1.6	-1.4	-1.4	-1.2	-1.6	2.2
-CH ₂ Br	4.0	1.1	-0.9	1.3	0.5	-0.1	0.3	-4.6	-2.8	0.1
-CH ₂ OH	8.2	-0.9	-0.6	0.1	0.5	-0.3	0.1	-4.5	-2.6	0.0
-CF ₃		-1.3	-1.8	5.0	1.0	0.8	2.0	-3.4	1.0	-3.9
H -F	31.5	-16.1	0.1	-3.8	0.1	1.4	0.7	-7.1	-9.3	2.1
a -Cl	3.9	0.2	-0.2	-0.9	0.2	3.1	0.8	-3.6	-2.8	1.0
I -Br	-5.4	3.6	-0.2	-0.5	-0.1	0.4	1.0	-1.3	-2.0	0.6
-I	-28.4	12.3	1.7	1.7	1.4	1.6	2.6	4.4	1.3	1.3
O -OH	23.5	-17.2	-0.1	-7.3	-0.4	0.5	0.3	-6.6	-9.3	1.0
-OCH ₃	27.3	-22.3	-0.2	-7.9	-0.7	0.3	-0.9	-6.1	-8.1	0.8
-OCOCH ₃	18.6	-7.9	-0.6	-2.1	0.0	0.4	0.4	-6.9	-6.9	0.9
N -NH ₂	14.0	-16.5	0.3	-9.3	0.3	-0.3	-1.3	-7.3	-10.2	0.6
-N(CH ₃) ₂	23.7	-11.2	0.6	-4.6	1.0	0.4	-0.3	-3.2	-3.9	2.1
-NH ₃ ⁺	-3.8	-4.6	-0.9	3.4	1.4	2.1	2.8	-9.0	-7.4	1.2
-NO ₂	18.5	-2.1	-2.0	6.5	0.5	1.3	3.4	-5.1	-8.7	0.6
-CN	-19.2	5.1	-2.4	3.8	-0.7	0.2	1.2	-4.5	-2.8	-2.2
O -CHO	2.9	10.8	-1.4	6.7	0.2	0.6	2.7	-3.5	-3.6	-0.3
 -COCH ₃	6.9	2.9	-1.7	4.9	0.3	0.4	2.0	-2.0	-3.5	0.2
C -COOH	-1.5	3.6	-2.4	4.3	-0.6	-0.9	0.6	-3.2	-3.2	-0.8
/\ -COOCH ₃	-0.9	4.5	-1.2	5.4	0.7	0.5	1.9	-1.8	-1.9	0.5
-CON(CH ₃) ₂	6.8	-2.1	-0.8	0.9	0.4	0.4	1.0	0.1	-4.1	-0.2
-COCl	1.2	10.6	-0.5	9.3	1.9	2.1	4.5	-2.1	-2.1	1.0
-Si(CH ₃) ₃	9.8	5.1	-0.4	1.7	1.2	-0.8	-0.7	0.1	3.8	0.2



Effect of Substituents in Position 2 on the ^{13}C Chemical Shifts of Monosubstituted Naphthalenes (in ppm relative to TMS)



for X: H $\delta_{\text{C}1} = 128.0$

$\delta_{\text{C}2} = 125.9$

$\delta_{\text{C}9} = 133.6$

Substituent X	C-1	C-2	C-3	C-4	C-5	C-6	C-7	C-8	C-9	C-10
C -CH ₃	-1.3	9.3	2.0	-0.8	-0.5	-1.1	-0.2	-0.6	-0.1	-2.0
-C(CH ₃) ₃	-3.3	22.5	-3.0	-0.4	0.0	-0.7	-0.2	-0.6	0.4	-1.3
-CH ₂ Br	-1.7	9.0	1.9	-0.4	-0.5	0.7	0.3	0.6	-0.6	-0.7
-CH ₂ OH	-2.7	12.3	-4.4	-0.1	-0.4*	-0.2*	0.1*	-0.2*	-0.3	-0.8
-CF ₃	-2.0		-4.2	1.1*	0.1*	2.4*	1.5	1.1	-1.1	1.3
H -F	-17.0	34.9	-9.6	2.4	0.0	-0.7	1.1	-0.6	0.7	-3.0
a -Cl	-1.4	5.7	0.8	1.5	-0.2	0.2	1.1	-1.1	0.7	-1.9
l -Br	1.8	-6.2	3.1	1.5	-0.3	0.2	0.8	-1.1	-2.0	0.7
-I	9.2	-34.1	9.0	2.3	0.5	1.3	1.5	-0.6	2.1	-0.8
O -OH	-18.6	27.3	-8.3	1.8	-0.3	-2.4	0.5	-1.7	0.9	-4.7
-OCH ₃	-22.2	31.8	-7.1	1.5	-0.3	-2.2	0.5	-1.2	1.0	-4.3
-OCOCH ₃	-9.5	22.5	-4.8	1.3	-0.4	-0.3	0.6	-0.4	0.1	-2.2
N -NH ₂	-20.6	16.7	-8.9	-0.2	-1.6	-4.8	-0.9	-3.5	-0.1	-7.0
-N(CH ₃) ₂	-21.1	23.6	-8.8	1.2	0.0	-3.4	0.7	-1.1	2.4	-5.9
-NH ₃ ⁺	-5.9	-0.3	-6.5	3.2	0.2	2.3	2.0	0.2	0.1	-0.3
-NO ₂	-3.4	20.0	-6.7	1.7	0.1	4.0	2.2	2.1	-1.1	2.4
-CN	5.8	-16.7	0.1	1.0	-0.2	3.0	1.6	0.2	-1.6	0.7
O -CHO	6.2	7.9	-3.6	0.8	-0.3	2.9	0.9	1.8	2.4	-1.4
 -COCH ₃	1.9	8.3	-2.2	0.2	-0.4	2.3	0.7	1.4	1.8	-1.3
C -COOH	2.7	2.4	-0.6	0.2	-0.3	2.4	0.9	1.3	-1.3	1.5
/\ -COOCH ₃	3.0	1.8	-0.5	0.2	-0.1	2.4	0.9	1.4	-1.0	1.9
-COCl	2.5	9.1	-0.7	0.2*	-0.4	2.2*	0.8	1.2		-1.4
-Si(CH ₃) ₃	5.8	11.9	3.9	-1.0	0.1	0.3	-0.2	0.1	-0.5	0.2

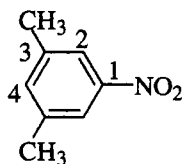
* assignment uncertain



Estimation of ^{13}C Chemical Shifts of Multiply Substituted Benzenes and Naphthalenes

The ^{13}C chemical shifts of multiply substituted benzenes and naphthalenes can be estimated using the substituent effects in the corresponding monosubstituted hydrocarbons.

Example: Estimation of the chemical shifts for 3,5-dimethylnitrobenzene



C-1 base value	128.5
$Z_1(\text{NO}_2)$	19.9
$2 Z_3(\text{CH}_3)$	-0.2
estimated	148.2
exp	148.5

C-2 base value	128.5
$Z_2(\text{NO}_2)$	-4.9
$Z_2(\text{CH}_3)$	0.7
$Z_4(\text{CH}_3)$	-3.0
estimated	121.3
exp	121.7

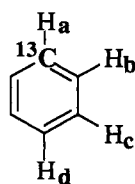
C-3 base value	128.5
$Z_1(\text{CH}_3)$	9.2
$Z_3(\text{CH}_3)$	-0.1
$Z_3(\text{NO}_2)$	0.9
estimated	138.5
exp	139.6

C-4 base value	128.5
$2 Z_2(\text{CH}_3)$	1.4
$Z_4(\text{NO}_2)$	6.1
estimated	136.0
exp	136.2

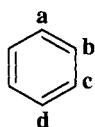
Larger discrepancies between estimated and experimental values are to be expected if the substituents are *ortho* to each other or if strongly electron-donating and electron-accepting groups occur simultaneously.

4.5.2 Coupling Constants

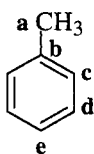
^{13}C - ^1H Coupling Constants ($|J|$ in Hz)



	In benzene:	In derivatives:
$^1J_{\text{C}_a\text{H}_a}$	159.0	
$^2J_{\text{C}_a\text{H}_b}$	1.0	1-4
$^3J_{\text{C}_a\text{H}_c}$	7.6	7-10
$^4J_{\text{C}_a\text{H}_d}$	-1.3	

¹³C-¹³C Coupling Constants ($|^1J_{CC}|$ in Hz)

$^1J_{ab}$	57.0
$^2J_{ac}$	2.5
$^3J_{ad}$	10.0



$^1J_{ab}$	44.2
$^2J_{ac}$	3.1
$^3J_{ad}$	3.8
$^4J_{ae}$	0.9

**4.5.3
References**

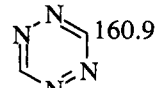
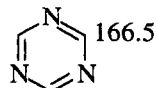
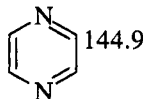
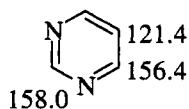
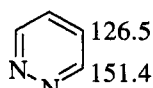
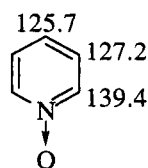
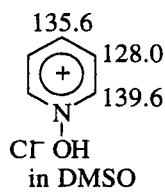
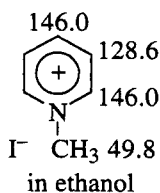
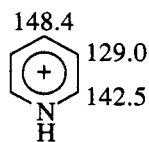
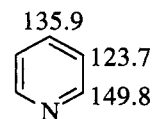
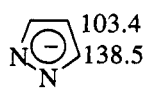
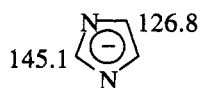
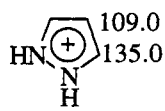
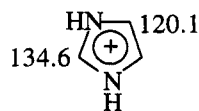
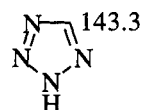
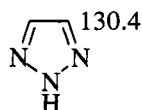
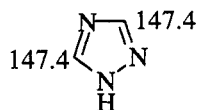
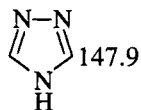
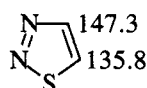
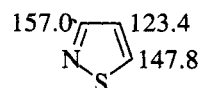
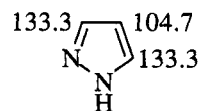
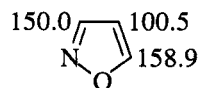
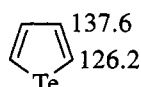
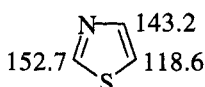
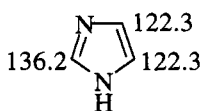
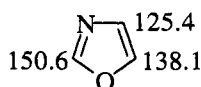
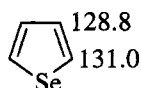
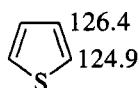
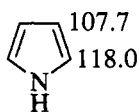
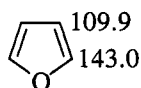
- [1] P.E. Hansen, ¹³C NMR of polycyclic aromatic hydrocarbons. A review, Org. Magn. Reson. **1979**, 12, 109.



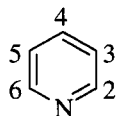
4.6 Heteroaromatic Compounds

4.6.1 Chemical Shifts

^{13}C Chemical Shifts of Heteroaromatic Compounds
(δ in ppm relative to TMS)



Effect of Substituents on the ^{13}C Chemical Shifts of Mono-substituted Pyridines (in ppm relative to TMS)



$$\delta_{\text{C-2}} = 149.8 + Z_{\text{i},2}$$

$$\delta_{\text{C-3}} = 123.7 + Z_{\text{i},3}$$

$$\delta_{\text{C-4}} = 135.9 + Z_{\text{i},4}$$

$$\delta_{\text{C-5}} = 123.7 + Z_{\text{i},5}$$

$$\delta_{\text{C-6}} = 149.8 + Z_{\text{i},6}$$

Substituent in position 2 or 6	$Z_{22} = Z_{66}$	$Z_{23} = Z_{65}$	$Z_{24} = Z_{64}$	$Z_{25} = Z_{63}$	$Z_{26} = Z_{62}$
H -H	0.0	0.0	0.0	0.0	0.0
C -CH ₃	8.6	-0.5	0.3	-3.0	-0.7
-CH ₂ CH ₃	13.7	-1.7	0.4	-2.8	-0.6
-CH=CH ₂	5.9	-1.3	1.1	-2.5	-0.3
-phenyl	7.7	-1.6	0.8	-3.2	0.2
H -F	13.9	-14.0	5.4	-2.5	-2.0
a -Cl	1.8	0.8	2.8	-1.4	0.0
I -Br	-7.5	4.6	2.6	-1.1	0.5
-I	-31.6	11.3	1.7	-0.8	1.0
O -OH	15.5	-3.6	-1.1	-17.0	-8.2
-OCH ₃	14.3	-12.7	2.6	-7.1	-2.9
-O-phenyl	13.9	-12.2	3.5	-5.3	-2.0
-OCOCH ₃	7.6	-7.3	3.4	-1.8	-1.6
N -NH ₂	8.4	-15.1	1.8	-9.7	-1.6
-NHCH ₃	10.9	-16.2	1.5	-11.3	-1.3
-N(CH ₃) ₂	9.6	-17.9	1.2	-12.3	-1.9
-NHCOCH ₃	1.4	-9.8	2.6	-3.9	-2.1
-NO ₂	6.9	-5.7	3.9	5.4	-0.8
-CN	-15.8	4.8	1.1	3.2	1.4
S -SH	30.4	10.7	2.1	-10.6	-12.1
-SCH ₃	10.2	-4.6	0.0	-2.2	-0.5
-S(=O)CH ₃	16.2	-4.4	2.2	0.9	-0.2
-S(=O) ₂ CH ₃	8.5	-2.6	2.4	3.7	0.3
O -CHO	3.0	-2.0	1.2	4.2	0.4
 -COCH ₃	3.8	-2.1	0.9	3.4	-0.8
C -COOH	-3.7	0.0	2.5	4.2	-1.7
/\ -COOCH ₃	-1.7	1.5	1.1	3.3	0.0
-CONH ₂	-0.3	-1.2	1.4	2.8	-1.5
-Si(CH ₃) ₃	18.6	5.0	-2.0	-1.1	0.3
-Sn(CH ₃) ₃	23.3	7.6	-2.7	-1.7	0.6
-Pb(CH ₃) ₃	33.4	9.2	-2.6	-2.3	1.1



Substituent in position 3 or 5		$Z_{32} = Z_{56}$	$Z_{33} = Z_{55}$	$Z_{34} = Z_{54}$	$Z_{35} = Z_{53}$	$Z_{36} = Z_{52}$
C	-H	0.0	0.0	0.0	0.0	0.0
	-CH ₃	1.3	8.9	0.0	-0.9	-2.3
	-CH ₂ CH ₃	-0.4	15.4	-0.8	-0.5	-2.7
	-phenyl	-1.4	12.8	-1.8	-0.3	-1.3
H	-F	-11.5	36.1	-13.2	0.8	-3.9
a	-Cl	-0.3	8.1	-0.4	0.6	-1.4
l	-Br	2.1	-2.7	2.7	1.1	-0.9
	-I	7.1	-28.5	8.9	2.3	0.3
O	-OH	-10.7	31.3	-12.4	1.2	-8.6
	-OCH ₃	-12.5	31.5	-15.9	0.1	-8.4
	-OCOCH ₃	-6.5	23.4	-7.0	-0.1	-3.2
N	-NH ₂	-11.9	21.4	-14.4	0.8	-10.8
	-NHCH ₃	-13.6	23.1	-18.2	0.6	-11.9
	-N(CH ₃) ₂	-14.0	23.3	-17.1	0.1	-11.6
	-CN	3.6	-13.8	4.2	0.5	4.2
S	-SH	-12.8	26.1	-11.3	7.3	-2.8
	-SCH ₃	-13.6	24.6	-11.7	10.6	-3.0
O	-CHO	2.4	7.8	-0.2	0.5	5.4
 	-COCH ₃	3.5	8.5	-0.7	-0.2	0.0
C	-COOH	-6.4	13.0	11.1	4.3	-6.0
/\	-COOCH ₃	-0.6	1.0	-0.5	-1.8	1.8
	-CONH ₂	2.7	5.9	1.1	1.2	-1.5
	-Si(CH ₃) ₃	2.7	9.1	3.0	-2.3	-1.2
	-Ge(CH ₃) ₃	3.9	12.8	4.2	-0.4	-0.1
	-Sn(CH ₃) ₃	5.9	13.0	7.1	0.1	-0.3
	-Sn(<i>n</i> -C ₄ H ₉) ₃	6.6	12.6	7.7	0.0	-0.4
	-Pb(<i>n</i> -C ₄ H ₉) ₃	7.1	21.7	8.5	0.9	-1.8



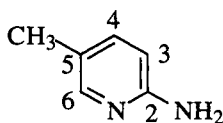
Substituent in position 4	$Z_{42} = Z_{46}$	$Z_{43} = Z_{45}$	Z_{44}
-H	0.0	0.0	0.0
C -CH ₃	0.5	0.7	10.6
-CH ₂ CH ₃	-0.1	-0.5	16.8
-CH(CH ₃) ₂	0.4	-1.9	21.2
-C(CH ₃) ₃	0.9	-2.6	23.9
-CH=CH ₂	0.3	-3.0	8.4
-phenyl	0.4	-2.2	12.2
H -F	2.7	-11.9	32.8
a -Br	3.0	3.3	-3.2
I -I	0.2	9.1	-30.8
O -OCH ₃	0.9	-13.9	29.0
-OCOCH ₃	1.7	-6.7	23.9
N -NH ₂	0.7	-13.8	19.3
-NHCH ₃	0.5	-15.9	19.8
-N(CH ₃) ₂	0.6	-16.3	19.2
-CN	2.1	2.1	-15.9
S -SH	-16.9	5.9	54.3
-SCH ₃	0.1	-3.3	14.6
O -CHO	1.7	-0.7	5.3
 -COCH ₃	1.6	-2.7	6.6
C -COOCH ₃	1.0	-0.8	1.4
/\ -CONH ₂	0.4	-0.9	6.2
-Si(CH ₃) ₃	-2.8	2.4	11.9
-Ge(CH ₃) ₃	-1.1	4.4	16.8
-Sn(CH ₃) ₃	-1.1	7.3	16.2
-Pb(CH ₃) ₃	-0.5	9.1	24.6



Estimation of ^{13}C Chemical Shifts of Multiply Substituted Pyridines

The ^{13}C chemical shifts in multiply substituted pyridines can be estimated using the substituent effects in the monosubstituted parent compound.

Example: Estimation of the chemical shifts for 2-amino-5-methylpyridine



C-2 base value	149.8
$Z_{22}(\text{NH}_2)$	8.4
$Z_{52}(\text{CH}_3)$	-2.3
estimated	155.9
exp	156.9

C-3 base value	123.7
$Z_{23}(\text{NH}_2)$	-15.1
$Z_{53}(\text{CH}_3)$	-0.9
estimated	107.7
exp	108.4

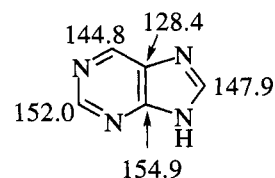
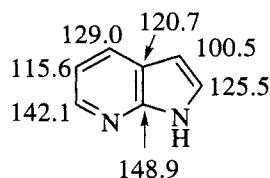
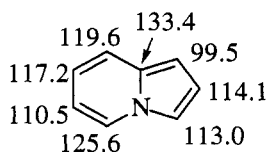
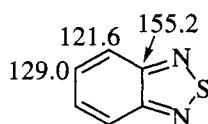
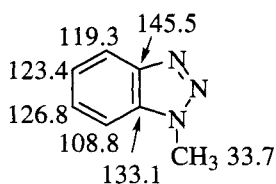
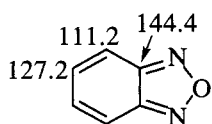
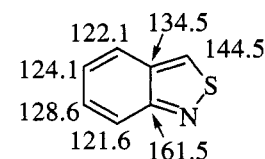
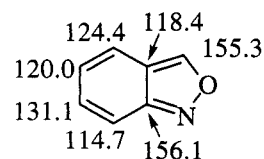
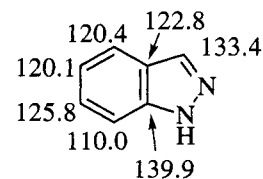
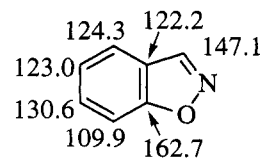
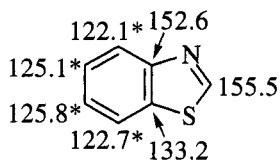
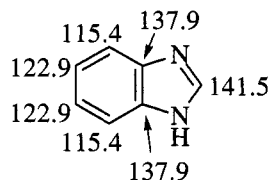
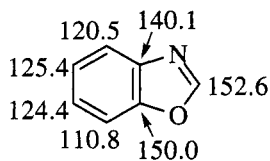
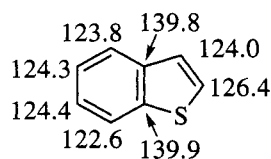
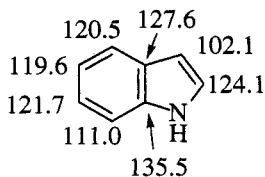
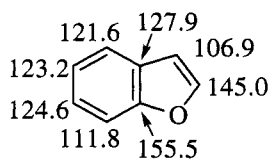
C-4 base value	135.9
$Z_{24}(\text{NH}_2)$	1.8
$Z_{54}(\text{CH}_3)$	0.0
estimated	137.7
exp	138.6

C-5 base value	123.7
$Z_{25}(\text{NH}_2)$	-9.7
$Z_{55}(\text{CH}_3)$	8.9
estimated	122.9
exp	122.5

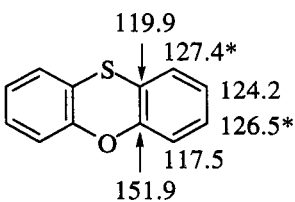
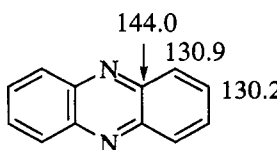
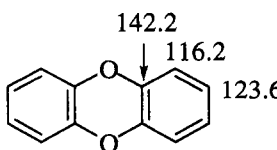
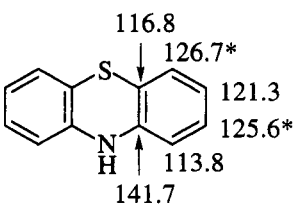
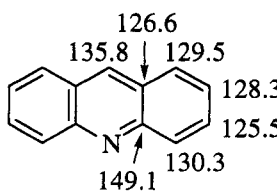
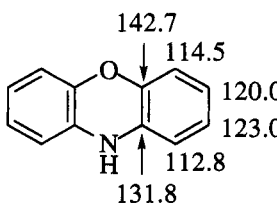
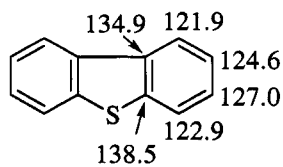
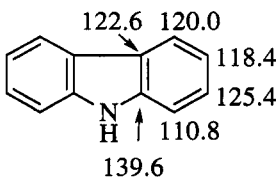
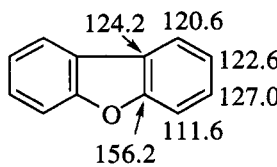
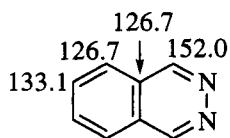
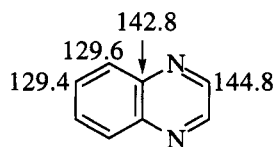
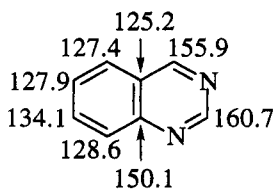
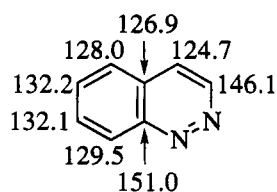
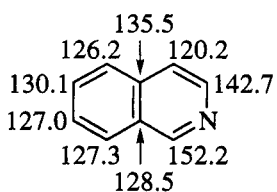
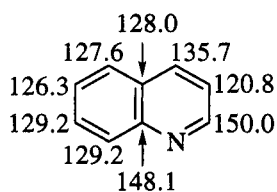
C-6 base value	149.8
$Z_{26}(\text{NH}_2)$	-1.6
$Z_{56}(\text{CH}_3)$	1.3
estimated	149.5
exp	147.6

Larger discrepancies between estimated and experimental values are to be expected if the substituents are *ortho* to each other and if strongly electron-donating and -accepting groups occur simultaneously. Also, tautomerization and zwitterion formation have large effects on ^{13}C chemical shifts.

¹³C Chemical Shifts of Condensed Heteroaromatic Rings
 (δ in ppm relative to TMS)



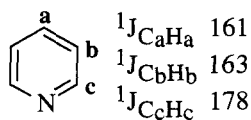
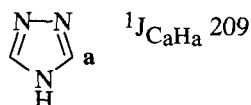
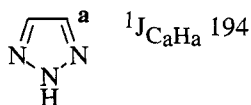
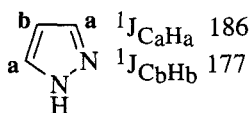
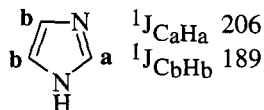
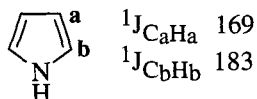
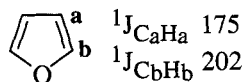
* assignment uncertain



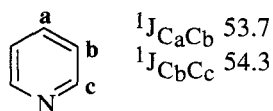
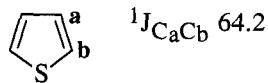
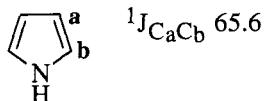
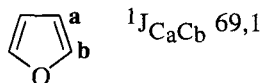
* assignment uncertain

4.6.2 Coupling Constants

^{13}C - ^1H Coupling Constants ($|J|$ in Hz)



^{13}C - ^{13}C Coupling Constants ($|J_{\text{CC}}|$ in Hz)




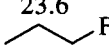
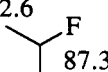
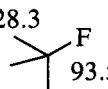
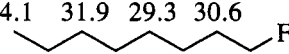

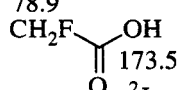
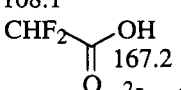
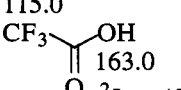
4.7 Halogen Compounds

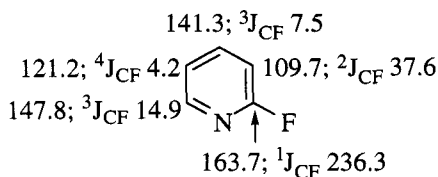
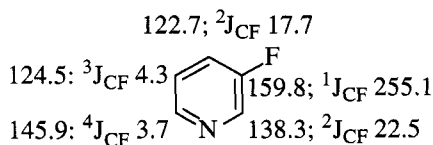
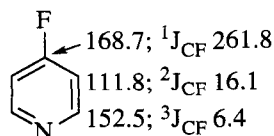
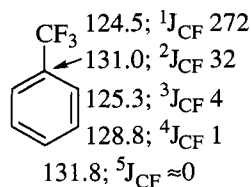
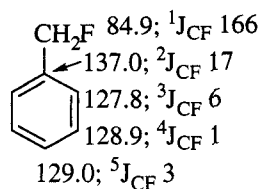
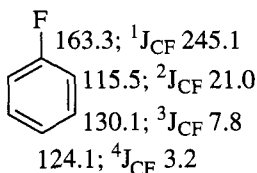
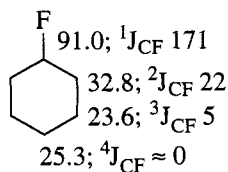
The additivity rules for estimating the ^{13}C chemical shifts of various skeletons can be applied to those haloalkanes that do not have more than one halogen atom at a given carbon atom. In all other cases, the simple linear models fail but correction terms for non-additivity are available for halomethanes and derivatives (see [1, 2]).

4.7.1 Fluoro Compounds

Fluorine in nature occurs 100% as ^{19}F , which exhibits a spin quantum number, $I = 1/2$. The signals of carbon atoms up to a distance of about four bonds are split by coupling to ^{19}F .

^{13}C Chemical Shifts and ^{19}F - ^{13}C Coupling Constants of Fluoro Compounds (δ in ppm relative to TMS, $|J|$ in Hz)

Hal	71.6 CH_3F	J_{CF} 161.9	109.0 CH_2F_2	J_{CF} 234.8	116.4 CHF_3	J_{CF} 274.3	118.5 CF_4	J_{CF} 259.2
	15.8 	80.1	$^2J_{\text{CF}}$ 19.5 23.6 	9.2 85.2 $^3J_{\text{CF}}$ 6.7 $^1J_{\text{CF}}$ 163.3	$^2J_{\text{CF}}$ 22.4 22.6 	87.3	28.3 	93.5
	14.1 31.9 29.3 30.6 	22.7 29.3 25.3 84.2 $^3J_{\text{CF}}$ 6.2 $^1J_{\text{CF}}$ 164.8	$^4J_{\text{CF}} \approx 0$ $^2J_{\text{CF}}$ 18.3	116.2 $\text{CF}_3\text{—CF}_3$	$^1J_{\text{CF}}$ 271 $^2J_{\text{CF}}$ 48.1	$^2J_{\text{CF}}$ 24.8 88.5 	147.7 $^1J_{\text{CF}}$ 267.2	
	$^1J_{\text{CF}}$ 177 78.9 	173.5 $^2J_{\text{CF}}$ 22	$^1J_{\text{CF}}$ 239 108.1 	167.2 $^2J_{\text{CF}}$ 28	$^1J_{\text{CF}}$ 283.2 115.0 	163.0 $^2J_{\text{CF}}$ 43.6		



Hal

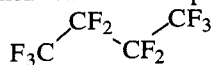
Estimation of ^{13}C Chemical Shifts of Linear Perfluoroalkanes
 (δ in ppm relative to TMS) [3]

$$\delta = 124.8 + \sum_i Z_i$$

Increments Z_i for the CF_2 - or CF_3 -substituent in position:

α	β	γ
-8.6	1.8	0.5

Example: Estimation of the chemical shifts in perfluorobutane



CF_3	base value	124.8	CF_2	base value	124.8
	1 α CF_2	-8.6		1 α CF_3	-8.6
	1 β CF_2	1.8		1 α CF_2	-8.6
	1 γ CF_3	0.5		1 β CF_3	1.8
	estimated	118.5		estimated	109.4
	exp	118.5		exp	109.3

4.7.2

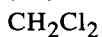
Chloro Compounds

 ^{13}C Chemical Shifts of Chloro Compounds (δ in ppm relative to TMS)

25.6



54.0



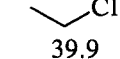
77.2



96.1

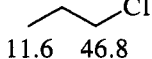


18.9



39.9

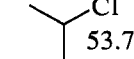
26.3



11.6

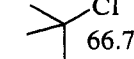
46.8

27.3



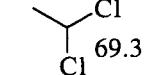
53.7

34.6



66.7

31.6

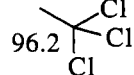


69.3

51.7

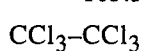


46.3

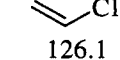


96.2

105.3

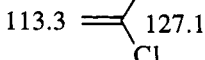


117.2



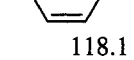
126.1

113.3



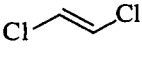
127.1

Cl



118.1

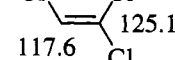
119.9



Cl

Hal

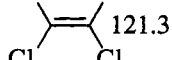
Cl



125.1

117.6

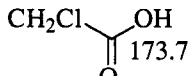
Cl



121.3

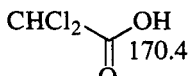
Cl

40.7



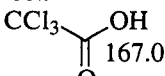
173.7

63.7

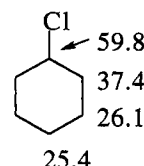


170.4

88.9



167.0

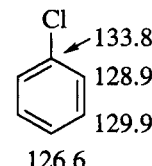


59.8

37.4

26.1

25.4

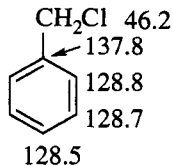


133.8

128.9

129.9

126.6



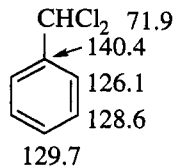
46.2

137.8

128.8

128.7

128.5



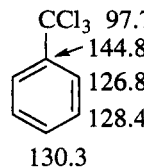
71.9

140.4

126.1

128.6

129.7



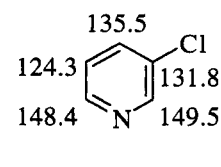
97.7

144.8

126.8

128.4

130.3



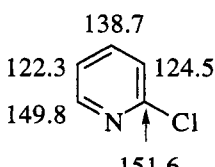
135.5

124.3

148.4

149.5

131.8



138.7

122.3

149.8

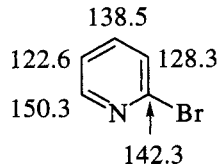
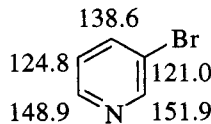
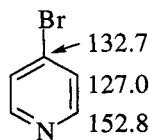
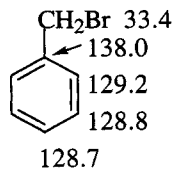
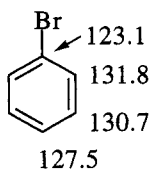
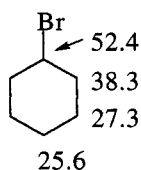
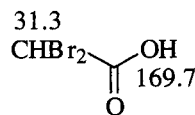
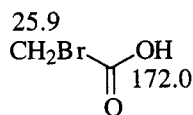
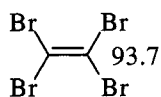
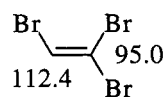
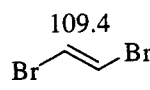
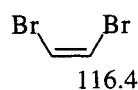
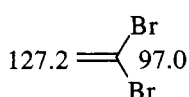
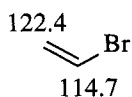
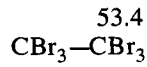
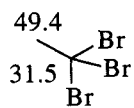
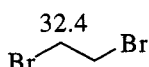
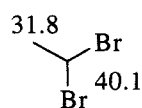
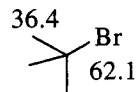
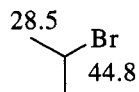
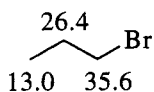
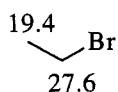
124.5

151.6

4.7.3 Bromo Compounds

¹³C Chemical Shifts of Bromo Compounds (δ in ppm relative to TMS)

9.6 <chem>CH3Br</chem>	21.4 <chem>CH2Br2</chem>	12.1 <chem>CHBr3</chem>	-28.7 <chem>CBr4</chem>
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Hal

4.7.4

Iodo Compounds

 ^{13}C Chemical Shifts of Iodo Compounds (δ in ppm relative to TMS)

-24.0



-54.0



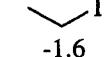
-139.9



-292.5

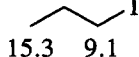


20.6



-1.6

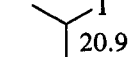
27.0



15.3

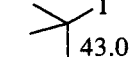
9.1

31.2



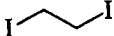
20.9

40.4

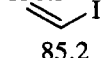


43.0

3.0



130.3

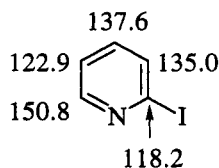
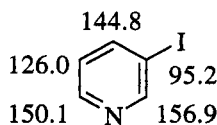
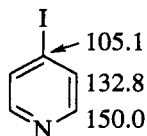
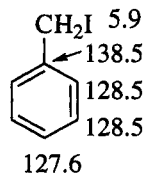
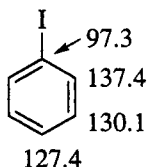
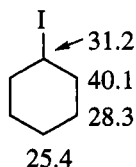
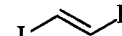


85.2



96.5

79.4



4.7.5

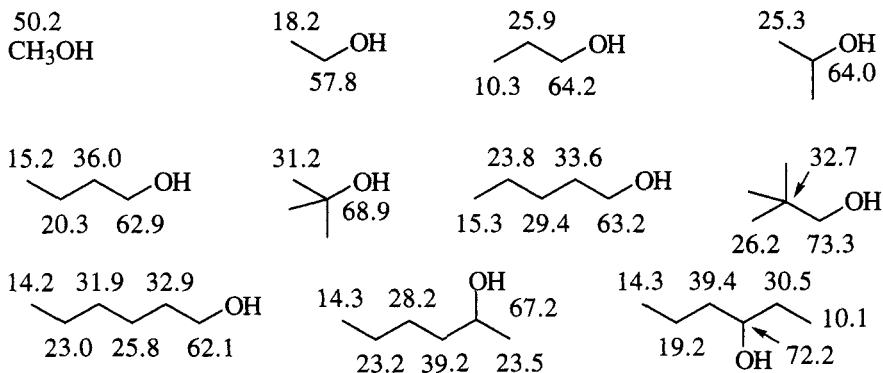
References

- [1] G.R. Somayajulu, J.R. Kennedy, T.M. Vickrey, B.J. Zwolinski, Carbon-13 chemical shifts for 70 halomethanes, *J. Magn. Reson.* **1979**, 33, 559.
- [2] A. Fürst, W. Robien, E. Pretsch, A comprehensive parameter set for the prediction of the ^{13}C NMR chemical shifts of sp^3 -hybridized carbon atoms in organic compounds, *Anal. Chim. Acta* **1990**, 233, 213.
- [3] D.W. Ovenall, J.J. Chang, Carbon-13 NMR of fluorinated compounds using wide-band fluorine decoupling, *J. Magn. Reson.* **1977**, 25, 361.

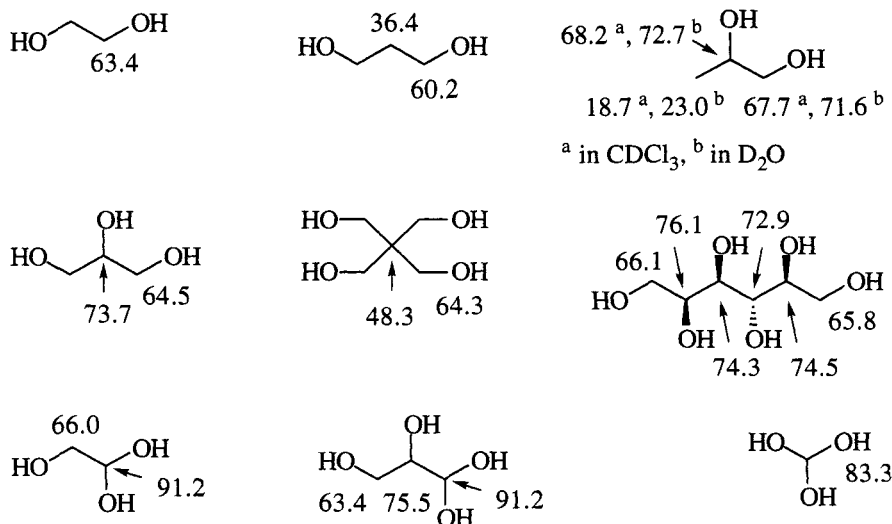
4.8 Alcohols, Ethers, and Related Compounds

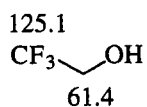
4.8.1 Alcohols

¹³C Chemical Shifts of Aliphatic Alcohols (δ in ppm relative to TMS)

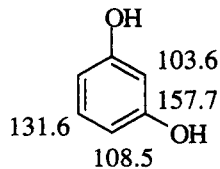
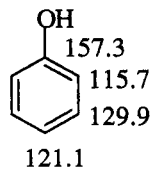
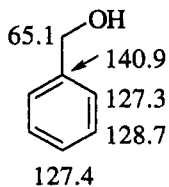
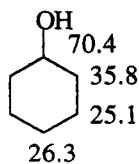
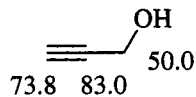
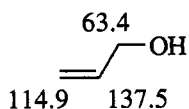
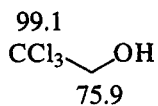
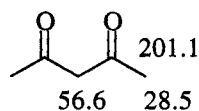
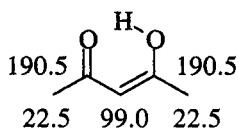
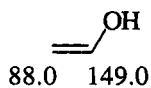


¹³C Chemical Shifts of Aliphatic Glycols and Polyols (δ in ppm relative to TMS)

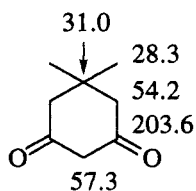
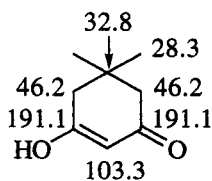


^{13}C Chemical Shifts of Alcohols (δ in ppm relative to TMS)

$^1J_{\text{CF}}$ 278 Hz
 $^2J_{\text{CF}}$ 35 Hz

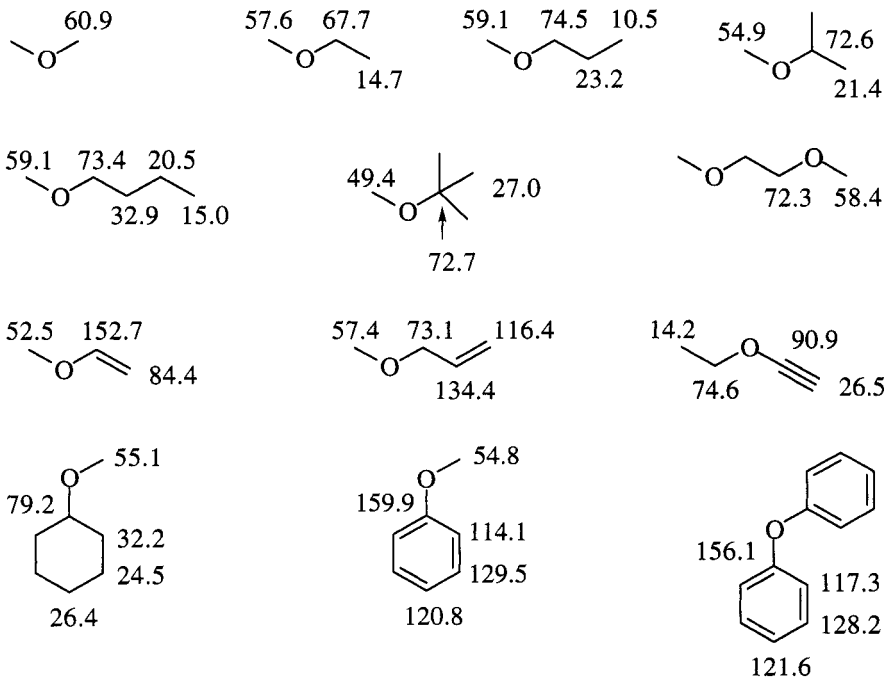
 **^{13}C Chemical Shifts of Enols (δ in ppm relative to TMS)**

O

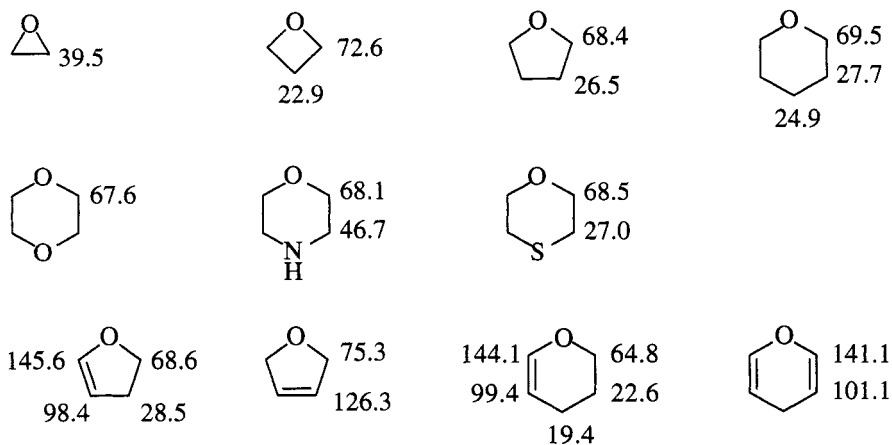


4.8.2 Ethers

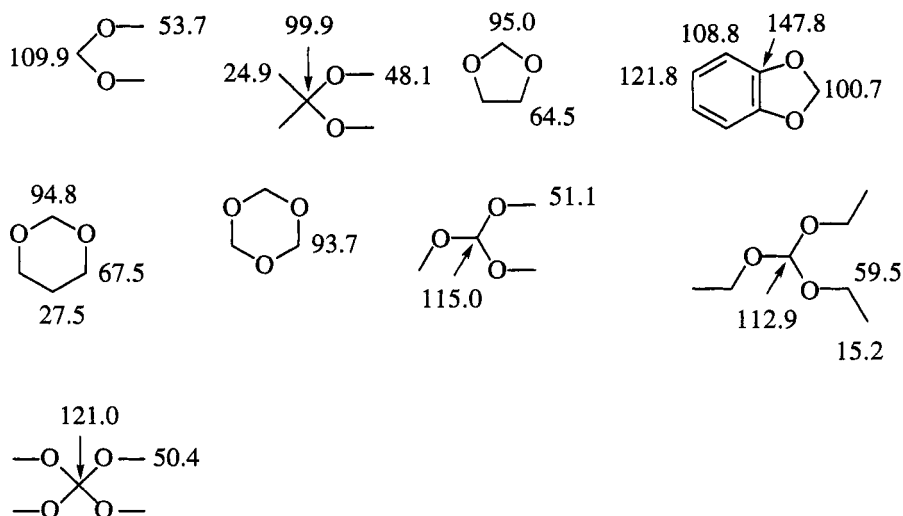
¹³C Chemical Shifts of Ethers (δ in ppm relative to TMS)



¹³C Chemical Shifts of Cyclic Ethers (δ in ppm relative to TMS)



^{13}C Chemical Shifts of Acetals, Ketals and Ortho Esters
 (δ in ppm relative to TMS)

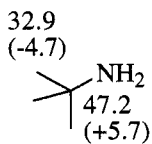
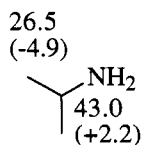
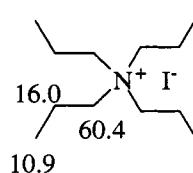
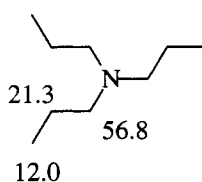
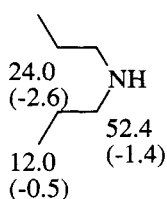
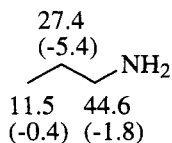
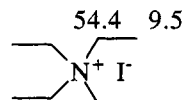
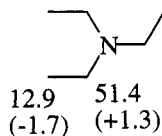
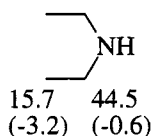
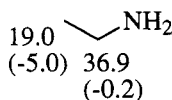
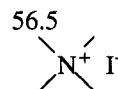
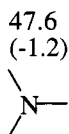
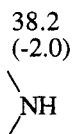
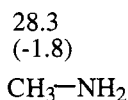


4.9 Nitrogen Compounds

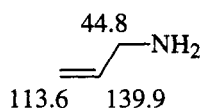
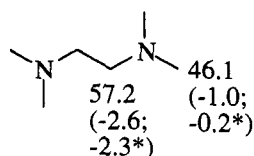
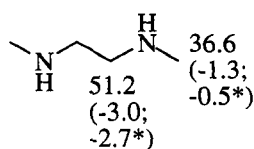
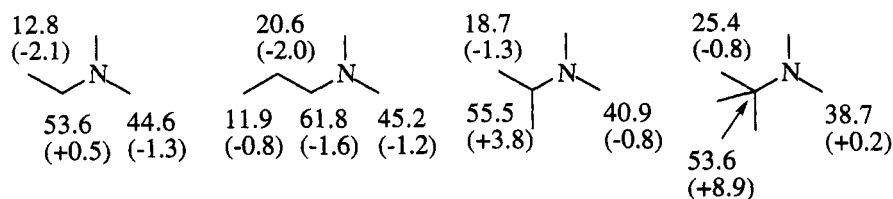
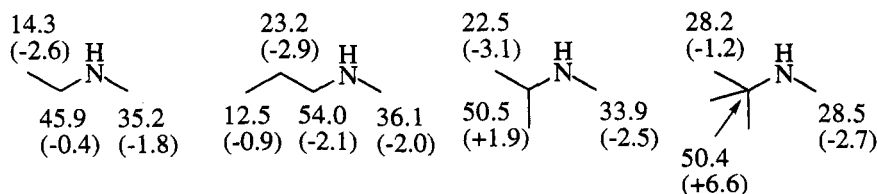
4.9.1 Amines

¹³C Chemical Shifts of Amines (δ in ppm relative to TMS) as well as Shifts Induced by Protonation (in parentheses: $\delta_{\text{amine hydrochloride}} - \delta_{\text{amine}}$, measured in D_2O)

The protonation of amines causes a shielding of the carbon atoms in the vicinity of the nitrogen. This shielding amounts to -2 ppm for an α -carbon atom, -3 to -4 for a β -carbon, and -0.5 to -1.0 ppm for a γ -carbon. The most frequent exceptions occur in branched systems: Tertiary and quaternary carbon atoms in the α -position are generally deshielded by protonation of the nitrogen ($\Delta\delta = +0.5$ to +9 ppm) [1].



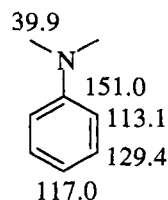
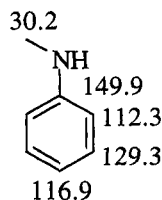
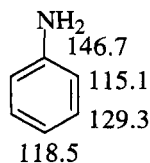
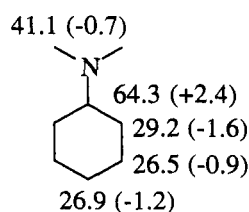
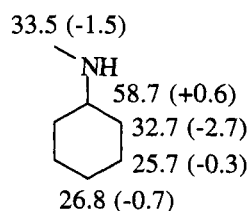
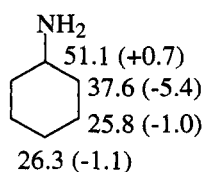
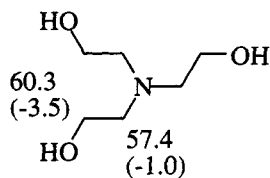
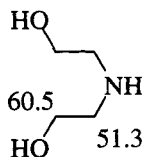
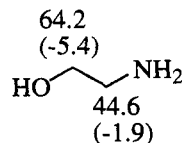
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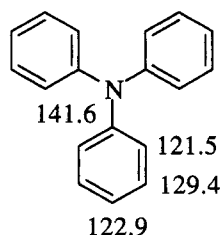
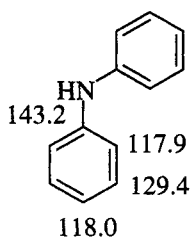
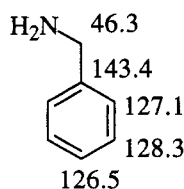


*doubly protonated form

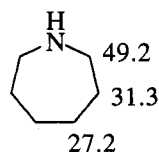
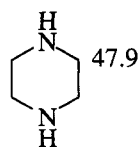
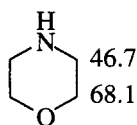
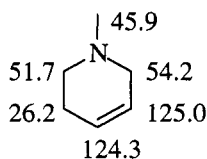
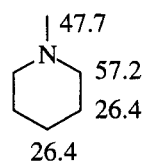
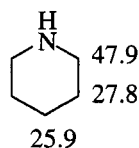
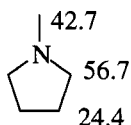
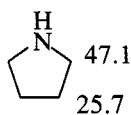
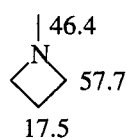
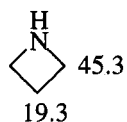
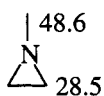
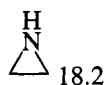
*doubly protonated form

N





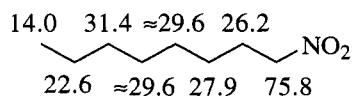
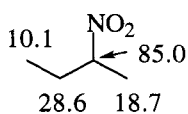
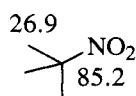
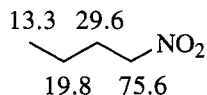
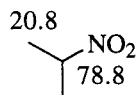
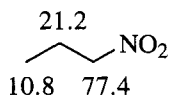
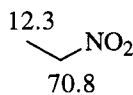
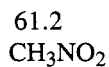
^{13}C Chemical Shifts of Cyclic Amines (δ in ppm relative to TMS)

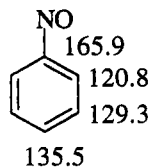
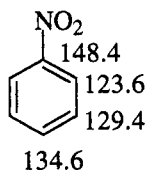
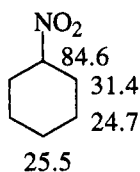


N

4.9.2 Nitro and Nitroso Compounds

^{13}C Chemical Shifts of Nitro and Nitroso Compounds (δ in ppm relative to TMS)

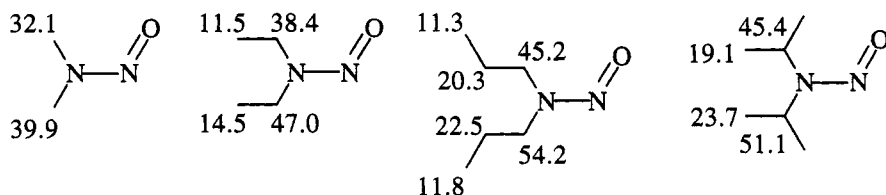




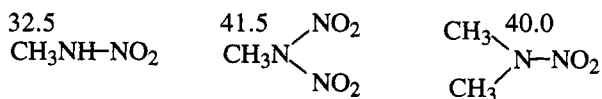
4.9.3

Nitrosamines and Nitramines

^{13}C Chemical Shifts of Nitrosamines (δ in ppm relative to TMS)



^{13}C Chemical Shifts of Nitramines (δ in ppm relative to TMS)

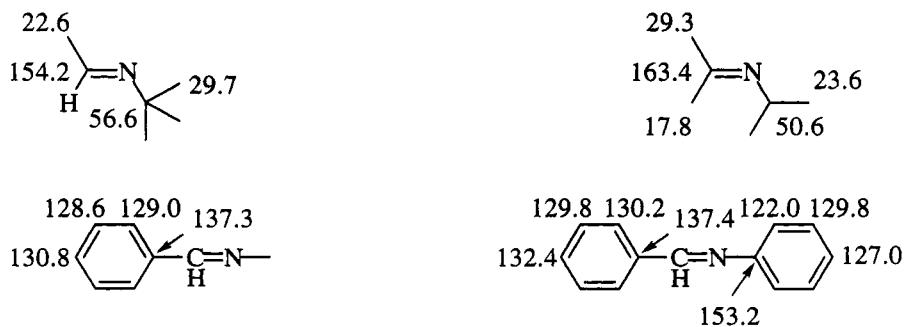


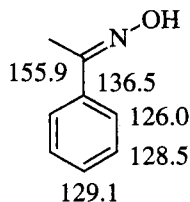
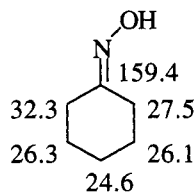
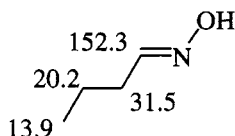
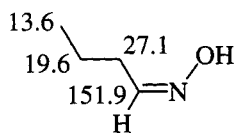
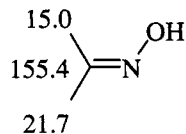
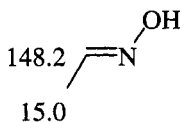
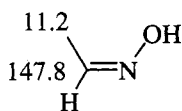
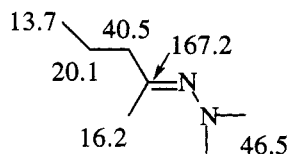
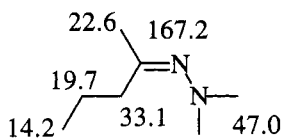
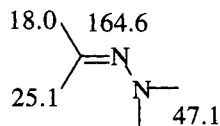
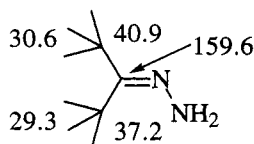
N

4.9.4

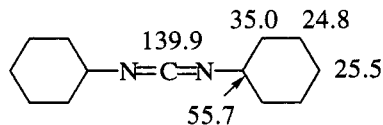
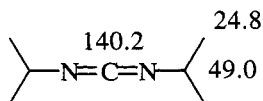
Imines and Oximes

^{13}C Chemical Shifts of Imines (δ in ppm relative to TMS)



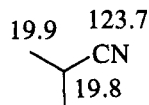
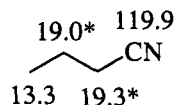
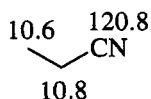
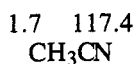
¹³C Chemical Shifts of Oximes (δ in ppm relative to TMS)**4.9.5
Hydrazones and Carbodiimides*****¹³C Chemical Shifts of Hydrazones (δ in ppm relative to TMS)***

N

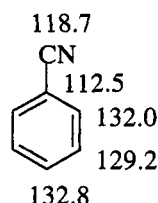
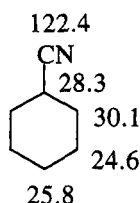
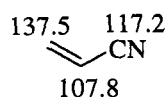
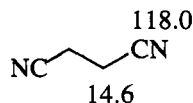
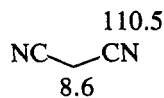
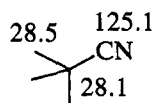
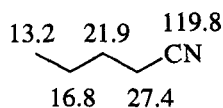
¹³C Chemical Shifts of Carbodiimides (δ in ppm relative to TMS)

4.9.6

Nitriles and Isonitriles

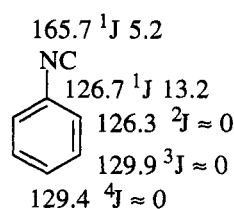
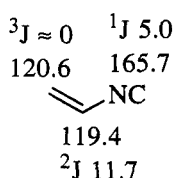
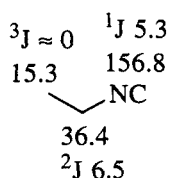
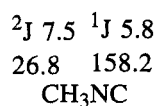
 ^{13}C Chemical Shifts of Nitriles (δ in ppm relative to TMS)

* assignment uncertain

 ^{13}C Chemical Shifts of Isonitriles(δ in ppm relative to TMS, $|J|_{\text{CN}}$ in Hz)

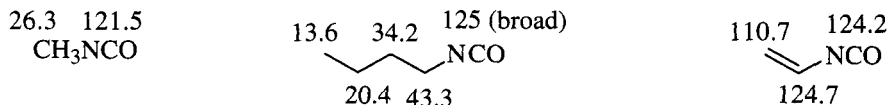
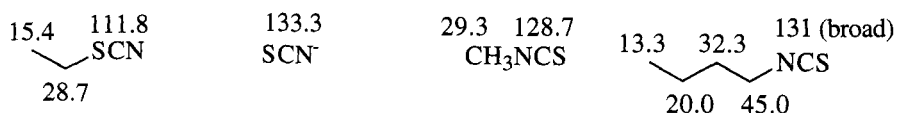
N

Because of the symmetrical electron distribution around the nitrogen atom, the ^{13}C - ^{14}N -coupling can be observed in the ^{13}C NMR spectra of isonitriles: triplets with relative intensities of 1:1:1 (spin quantum number of ^{14}N : $I = 1$, natural abundance 99.6%).



4.9.7

Isocyanates, Thiocyanates and Isothiocyanates

¹³C Chemical Shifts of Isocyanates (δ in ppm relative to TMS)*¹³C Chemical Shifts of Thiocyanates and Isothiocyanates (δ in ppm relative to TMS)*

4.9.8

References

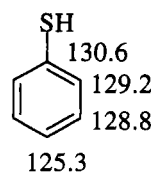
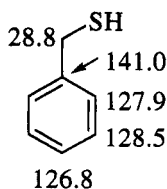
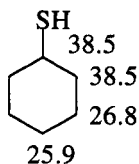
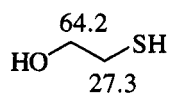
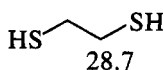
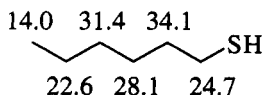
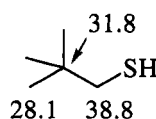
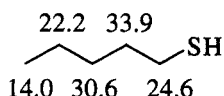
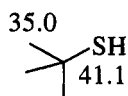
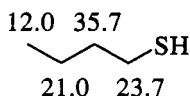
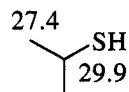
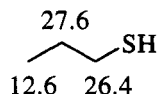
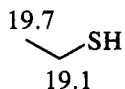
- [1] J.E. Sarneski, H.L. Surprenant, F.K. Molen, Ch.N. Reilley, Chemical shifts and protonation shifts in carbon-13 nuclear magnetic resonance studies of aqueous amines, *Anal. Chem.* **1975**, *47*, 2116.

4.10

Sulfur-Containing Functional Groups

4.10.1

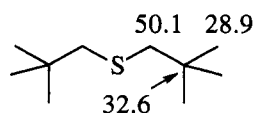
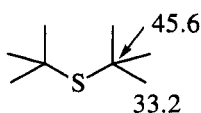
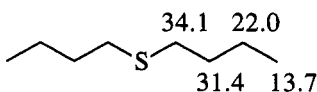
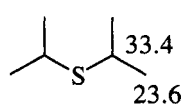
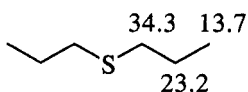
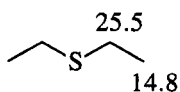
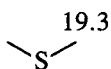
Thiols

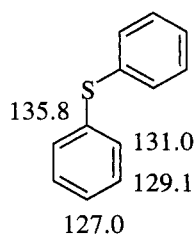
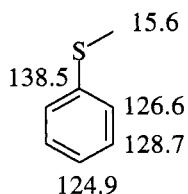
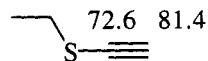
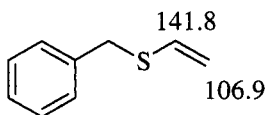
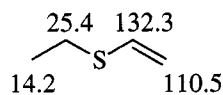
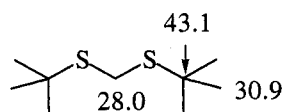
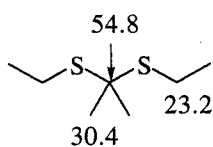
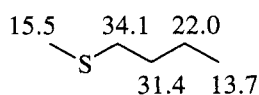
 ^{13}C Chemical Shifts of Thiols (δ in ppm relative to TMS)

S

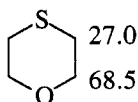
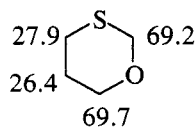
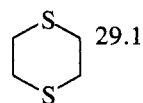
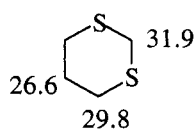
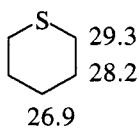
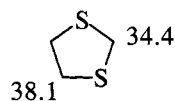
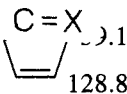
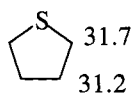
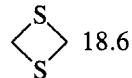
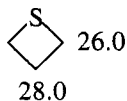
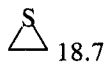
4.10.2

Sulfides

 ^{13}C Chemical Shifts of Sulfides (δ in ppm relative to TMS)



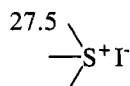
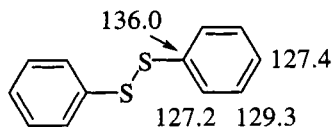
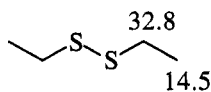
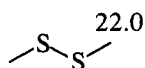
^{13}C Chemical Shifts of Cyclic Sulfides (δ in ppm relative to TMS)



S

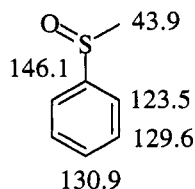
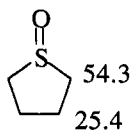
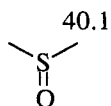
4.10.3

Disulfides and Sulfonium Salts

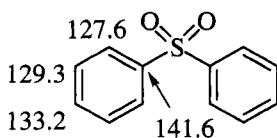
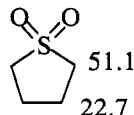
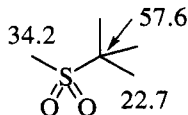
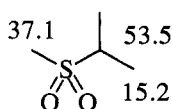
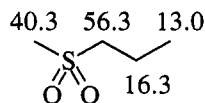
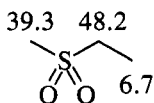
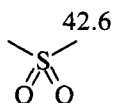
 ^{13}C Chemical Shifts of Disulfides and Sulfonium Salts(δ in ppm relative to TMS)

4.10.4

Sulfoxides and Sulfones

 ^{13}C Chemical Shifts of Sulfoxides and Sulfones(δ in ppm relative to TMS)

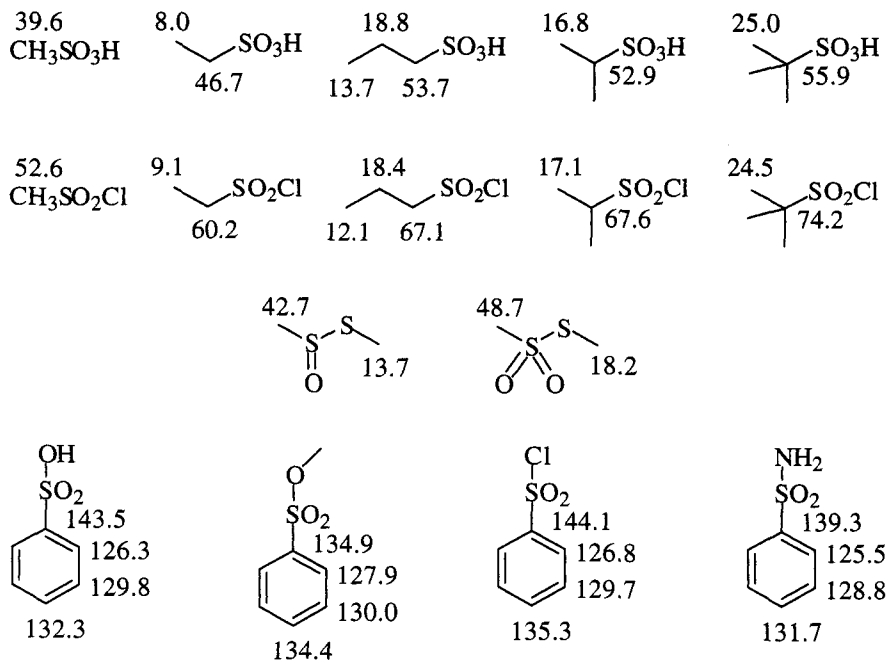
S



4.10.5

Sulfonic and Sulfinic Acids and Derivatives

¹³C Chemical Shifts of Sulfonic and Sulfinic Acids and Derivatives (δ in ppm relative to TMS)



4.10.6

Sulfurous and Sulfuric Acid Derivatives

S

¹³C Chemical Shifts of Sulfurous and Sulfuric Acid Derivatives (δ in ppm relative to TMS)



4.10.7

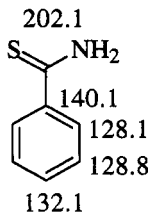
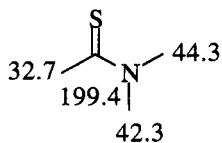
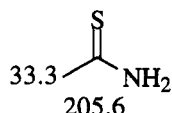
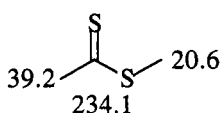
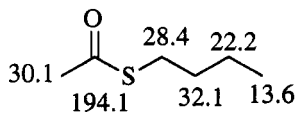
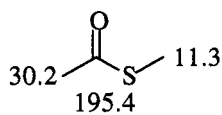
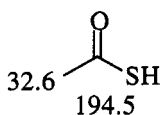
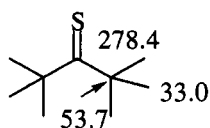
Sulfur-Containing Carbonyl Derivatives

 ^{13}C Chemical Shifts of Sulfur-Containing Carbonyl Derivatives
(δ in ppm relative to TMS)

The chemical shifts of thiocarbonyl groups are higher by about 30 ppm than those of the corresponding carbonyl groups:

$$\delta_{\text{C}=\text{S}} \approx 1.5 \delta_{\text{C}=\text{O}} - 57.5$$

Carbonyl groups of thiocarboxylic acids and their esters are deshielded by about 20 ppm with respect to the corresponding oxygen compounds.

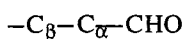


4.11 Carbonyl Compounds

4.11.1 Aldehydes

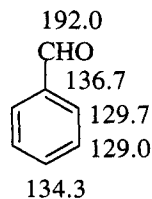
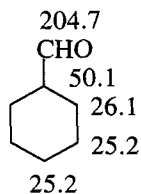
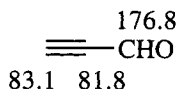
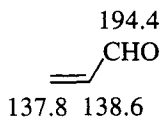
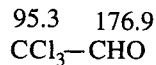
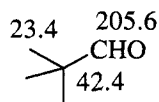
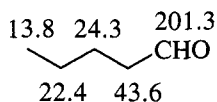
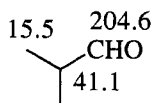
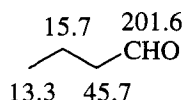
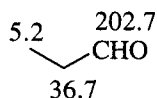
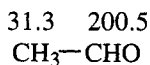
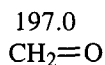
Additivity Rule for Estimating the ^{13}C Chemical Shifts of Aldehyde Carbonyl Carbon Atoms (δ in ppm relative to TMS)

$$\delta_{\text{C=O}} = 193.0 + \sum_i Z_i$$



Substituent i	Z_α	Z_β
$-\text{C}\equiv$	6.5	2.6
$-\text{CH}=\text{CH}_2$	-0.8	0.0
$-\text{CH}=\text{CH}-\text{CH}_3$	0.2	0.0
-phenyl	-1.2	0.0

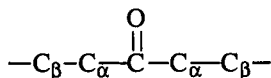
^{13}C Chemical Shifts of Aldehydes (δ in ppm relative to TMS)



4.11.2 Ketones

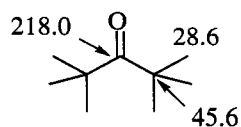
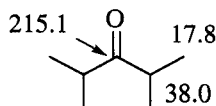
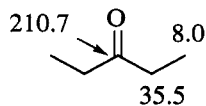
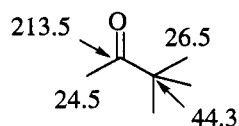
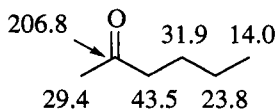
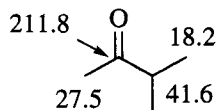
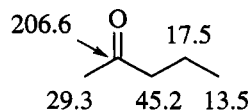
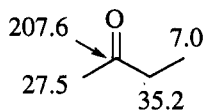
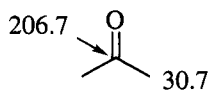
Additivity Rule for Estimating the ^{13}C Chemical Shifts of Ketone Carbonyl Carbon Atoms (δ in ppm relative to TMS)

$$\delta_{\text{C=O}} = 193.0 + \sum_i Z_i$$



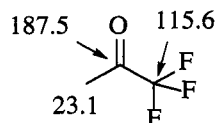
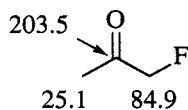
Substituent i	Z_α	Z_β
$-\text{C}\equiv$	6.5	2.6
$-\text{CH}=\text{CH}_2$	-0.8	0.0
$-\text{CH}=\text{CH}-\text{CH}_3$	0.2	0.0
-phenyl	-1.2	0.0

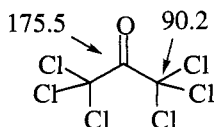
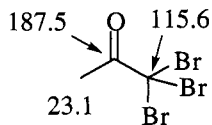
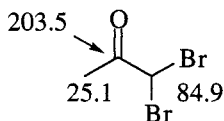
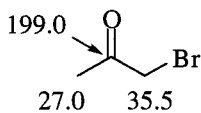
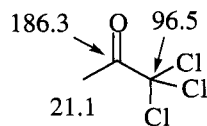
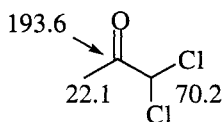
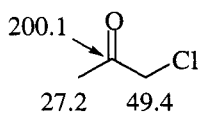
^{13}C Chemical Shifts of Aliphatic Ketones (δ in ppm relative to TMS)



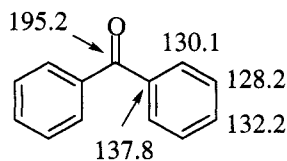
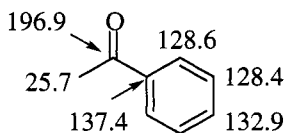
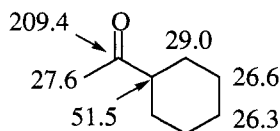
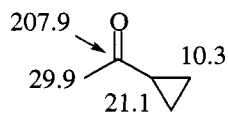
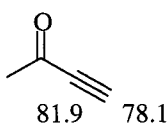
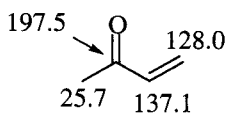
C=X

^{13}C Chemical Shifts of Halogenated Ketones
(δ in ppm relative to TMS)

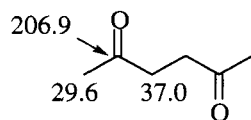
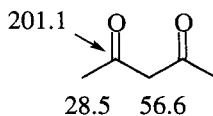
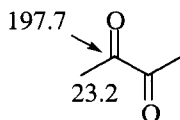




¹³C Chemical Shifts of Unsaturated and Alicyclic Ketones
(δ in ppm relative to TMS)



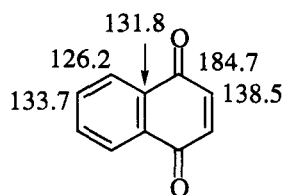
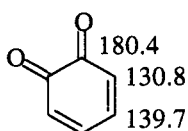
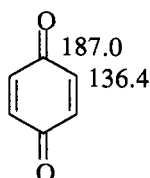
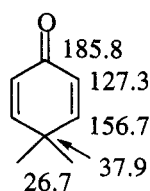
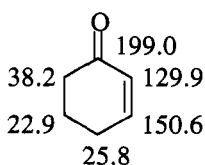
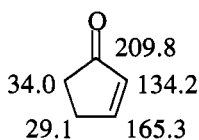
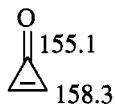
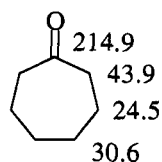
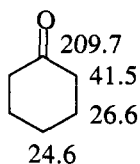
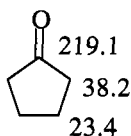
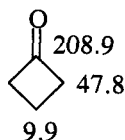
¹³C Chemical Shifts of Diketones (δ in ppm relative to TMS)



C=X

Enol form: see Chapter 4.8

^{13}C Chemical Shifts of Cyclic Ketones and Quinones
(δ in ppm relative to TMS)

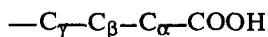


4.11.3
Carboxylic Acids and Carboxylates

Additivity Rule for Estimating the ^{13}C Chemical Shifts of Carboxyl Carbon Atoms (δ in ppm relative to TMS)








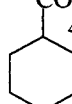
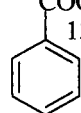

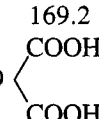
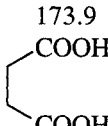
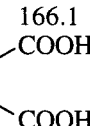
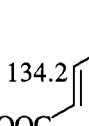
$$\delta_{\text{C=O}} = 166.0 + \sum_i Z_i$$

$\text{O}=\text{C}-\text{X}$



Substituent i	Z_α	Z_β	Z_γ
$-\text{C}\equiv$	11.0	3.0	-1.0
$-\text{CH}=\text{CH}_2$	5.0		
-phenyl	6.0	1.0	

¹³C Chemical Shifts of Carboxylic Acids (δ in ppm relative to TMS)

166.3 H-COOH	21.7 176.9 CH ₃ -COOH	9.6 180.4  COOH 28.5	18.7 179.4  COOH 13.7 36.2	
18.8 184.1  COOH 34.1	14.2 27.7 180.6  COOH 22.7 34.8		27.1 185.9  COOH 38.7	
171.7  COOH 133.1 128.3	156.5  COOH 78.6 74.0	182.1  COOH 43.7 29.6 26.2 26.6	172.6  COOH 130.6 130.1 128.4 133.7	
115.0 163.0 CF ₃ -COOH	40.7 173.7 CH ₂ Cl-COOH	63.7 170.4 CHCl ₂ -COOH	88.9 167.1 CCl ₃ -COOH	
160.1  COOH COOH	169.2 40.9  COOH COOH	173.9 28.9  COOH COOH	166.1 130.4  COOH COOH	166.6 134.2  COOH HOOC

¹³C Chemical Shifts of Carboxylate Anions*(δ in ppm relative to TMS; measured in water unless indicated otherwise)*

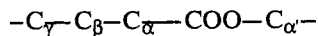
171.3 H-COO ⁻	24.4 182.6 20.8* 177.6* CH ₃ -COO ⁻ * solvent: CDCl ₃	11.1 185.1 10.6* 181.3* CH ₃ -CH ₂ -COO ⁻ 31.5 28.4* * solvent: CDCl ₃ /DMSO	188.6 CH ₃ -C(CH ₃) ₂ -COO ⁻ C = X
174.5 CH ₂ =CH-COO ⁻ 126.7 134.3		185.4 Cyclohexyl-COO ⁻ 47.2 30.9 26.9 26.9	177.6 Phenyl-COO ⁻ 138.2 133.1 130.7 133.1
45.0 175.9 CH ₂ Cl-COO ⁻		65.6 171.8 CHCl ₂ -COO ⁻	96.2 167.6 CCl ₃ -COO ⁻

4.11.4

Esters and Lactones

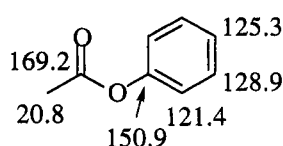
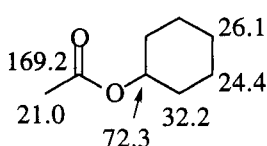
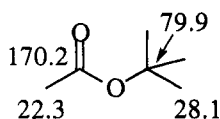
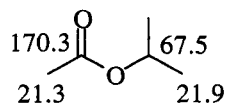
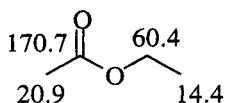
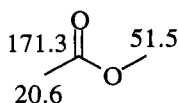
Additivity Rule for Estimating the ^{13}C Chemical Shifts of Ester Carbonyl Carbon Atoms (δ in ppm relative to TMS)

$$\delta_{\text{C=O}} = 166.0 + \sum_i Z_i$$

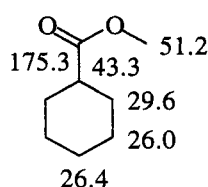
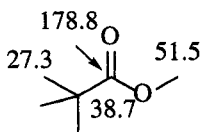
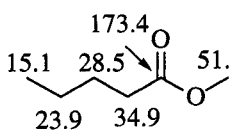
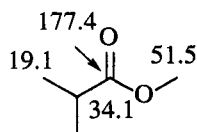
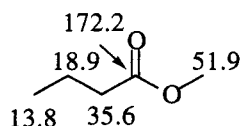
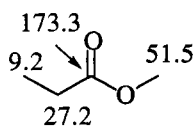
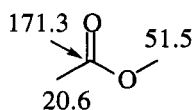
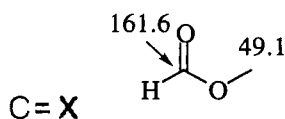


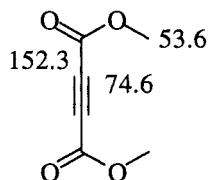
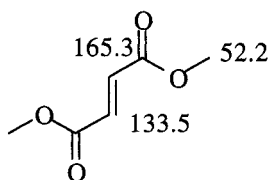
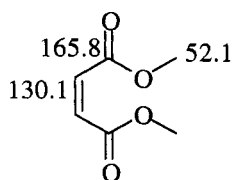
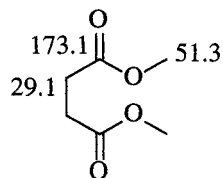
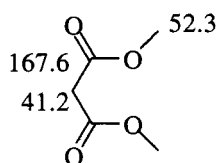
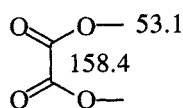
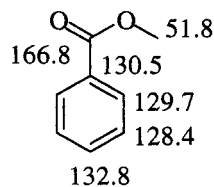
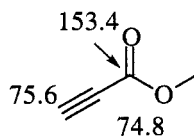
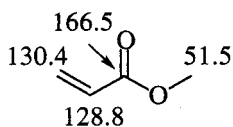
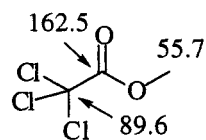
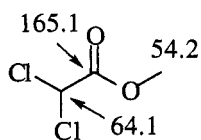
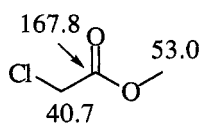
Substituent i	Z_α	Z_β	Z_γ	$Z_{\alpha'}$
$-\text{C}\equiv$	11.0	3.0	-1.0	-5.0
$-\text{CH}=\text{CH}_2$	5.0			-9.0
-phenyl	6.0	1.0		-8.0

^{13}C Chemical Shifts of Acetic Acid Esters (δ in ppm relative to TMS)

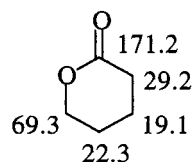
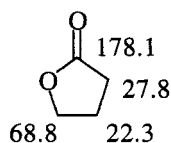
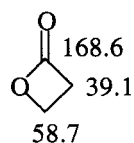


^{13}C Chemical Shifts of Methyl Esters (δ in ppm relative to TMS)

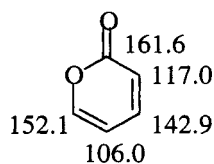
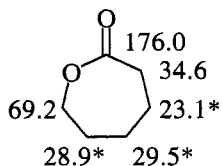




¹³C Chemical Shifts of Lactones (δ in ppm relative to TMS)



C = X



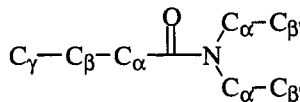
* assignment uncertain

4.11.5

Amides and Lactams

Additivity Rule for Estimating the ^{13}C Chemical Shifts of Amide Carbonyl Carbon Atoms (δ in ppm relative to TMS)

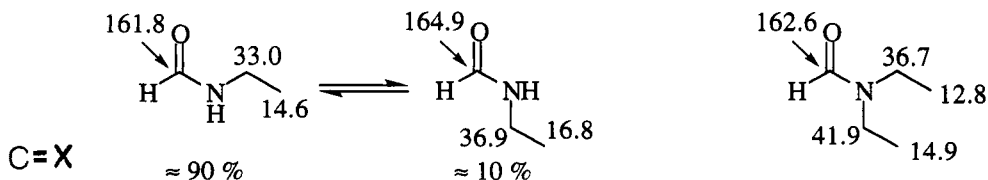
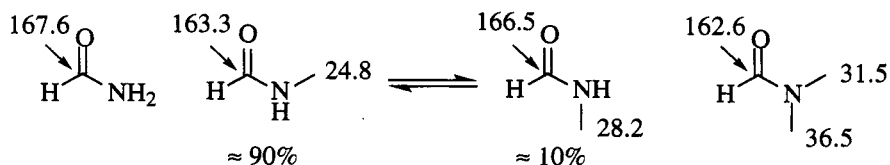
$$\delta_{\text{C=O}} = 165.0 + \sum_i Z_i$$



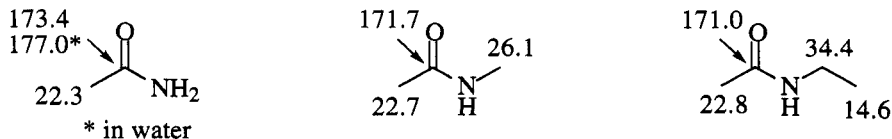
Substituent i	Z_α	Z_β	Z_γ	$Z_{\alpha'}$	$Z_{\beta'}$
$-\text{C}\equiv$	7.7	4.5	-0.7	-1.5	-0.3
$-\text{CH}=\text{CH}_2$	3.3				
-phenyl	4.7			-4.5	

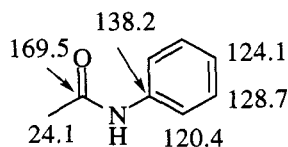
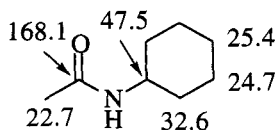
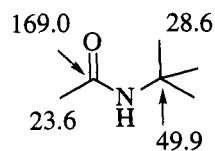
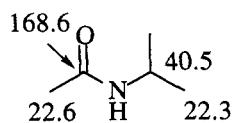
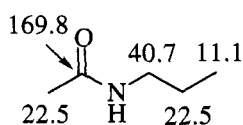
^{13}C Chemical Shifts of Amides (δ in ppm relative to TMS)

Formamides:

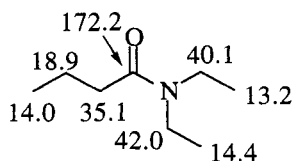
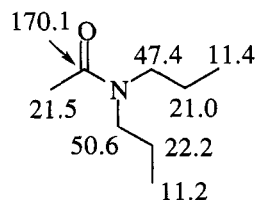
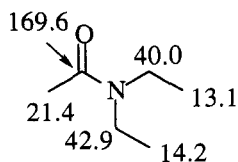
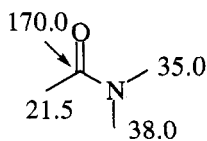


Primary and Secondary Acetamides:

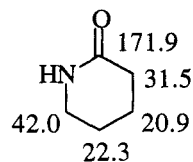
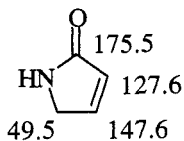
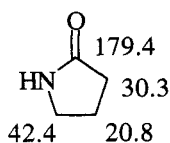




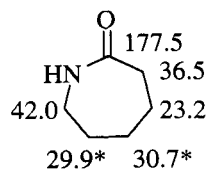
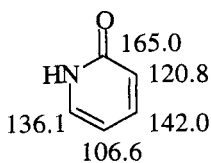
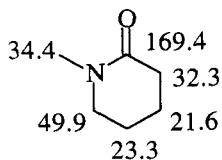
Tertiary Aliphatic Amides:



¹³C Chemical Shifts of Lactams (δ in ppm relative to TMS)



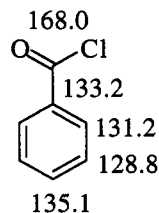
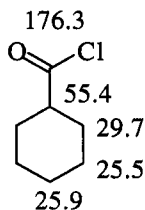
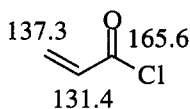
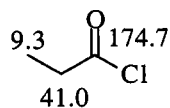
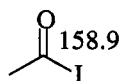
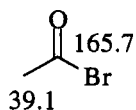
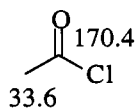
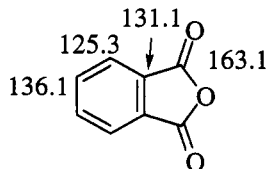
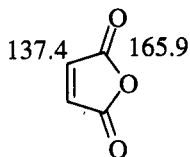
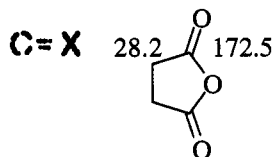
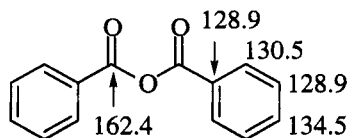
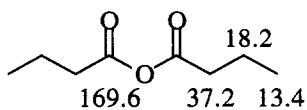
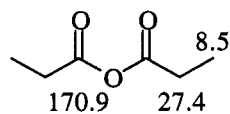
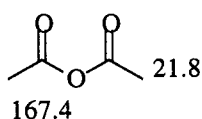
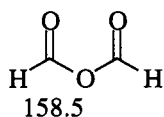
C=X

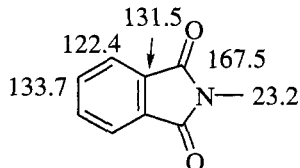
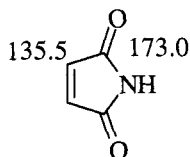
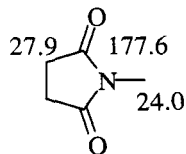
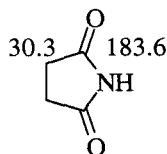
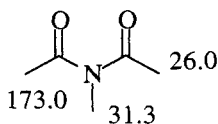
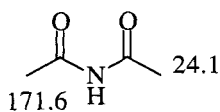
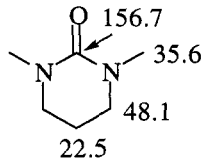
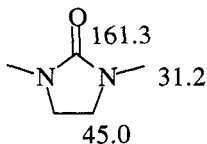
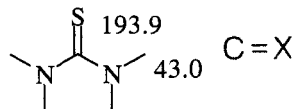
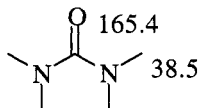
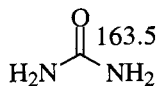
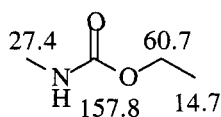
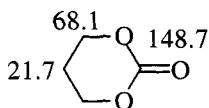
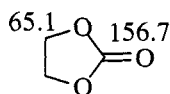
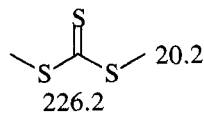
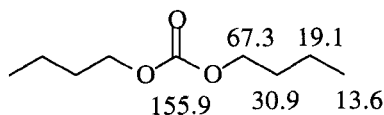
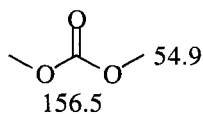
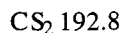
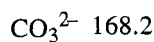
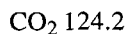
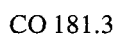


* assignment uncertain

4.11.6

Miscellaneous Carbonyl Derivatives

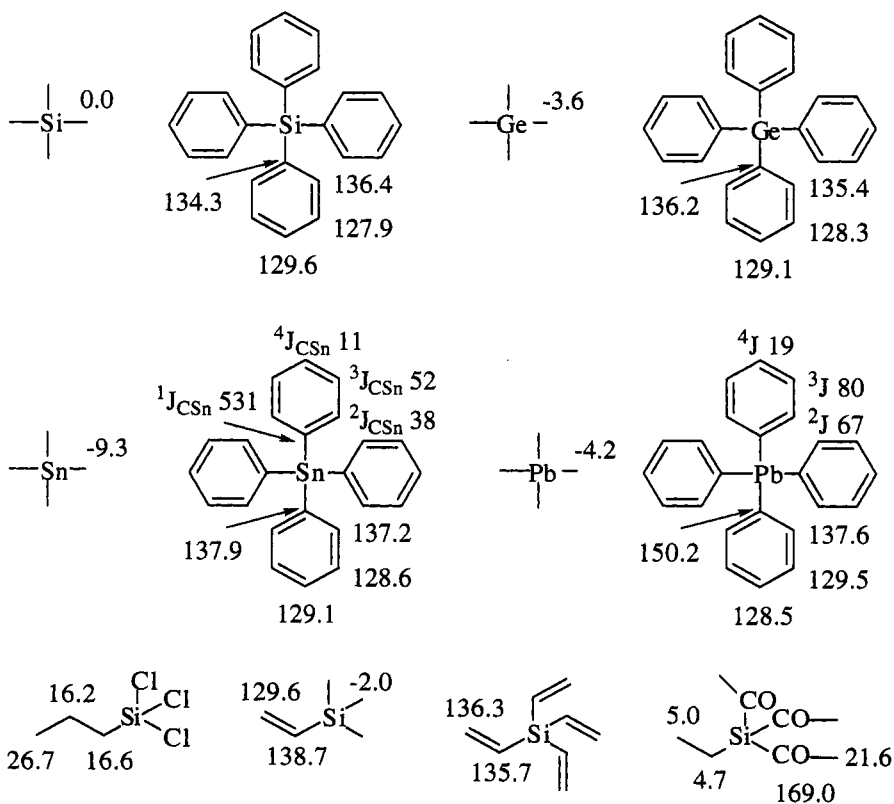
 ^{13}C Chemical Shifts of Carboxylic Acid Halides(δ in ppm relative to TMS) ^{13}C Chemical Shifts of Carboxylic Acid Anhydrides(δ in ppm relative to TMS)

¹³C Chemical Shifts of Carboxylic Acid Imides*(δ in ppm relative to TMS)****¹³C Chemical Shifts of Carbonic Acid Derivatives****(δ in ppm relative to TMS)*

4.12 Miscellaneous Compounds

4.12.1 Derivatives of Group IV Elements

^{13}C Chemical Shifts and Coupling Constants of Derivatives of Group IV Elements (δ in ppm relative to TMS, $|J|$ in Hz)

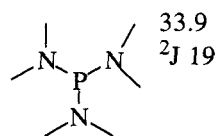
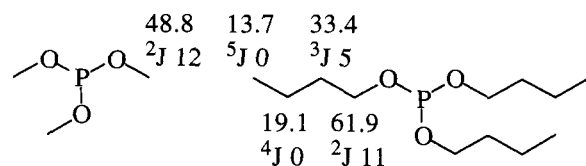
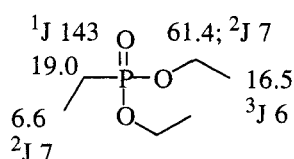
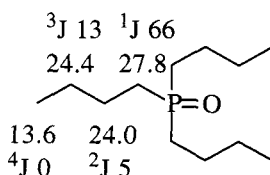
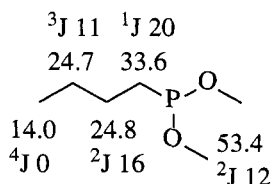
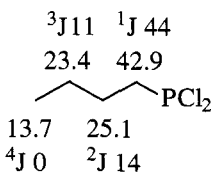
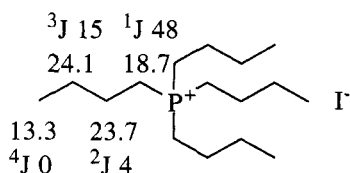
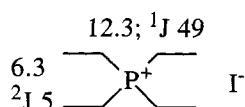
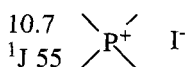
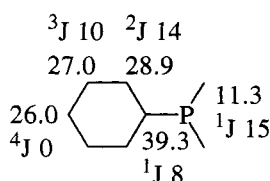
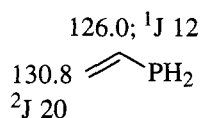
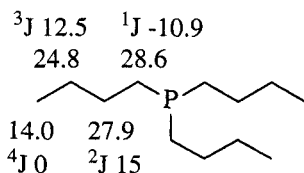
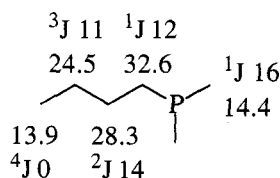


Misc.

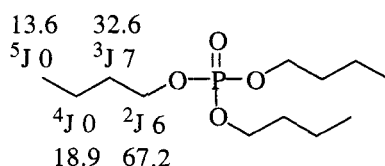
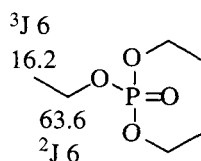
4.12.2

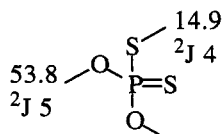
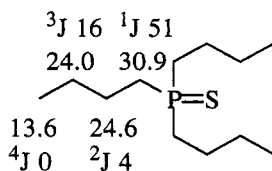
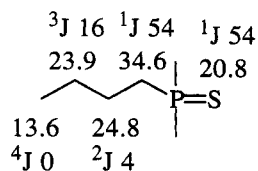
Phosphorus Compounds

¹³C Chemical Shifts and ³¹P-¹³C Coupling Constants of Aliphatic Phosphorus Compounds (δ in ppm relative to TMS, $|J|$ in Hz)

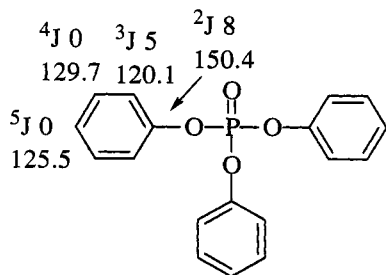
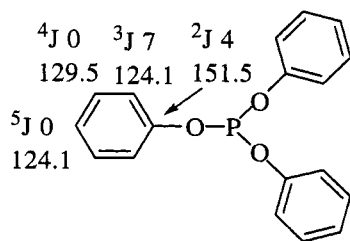
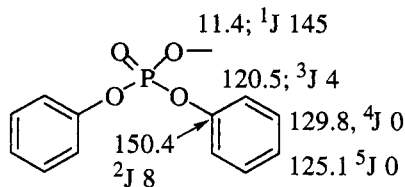
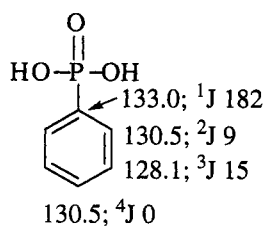
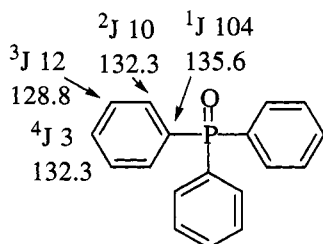
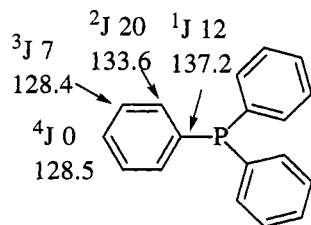


Misc.



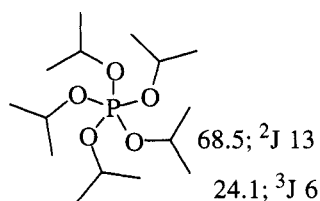
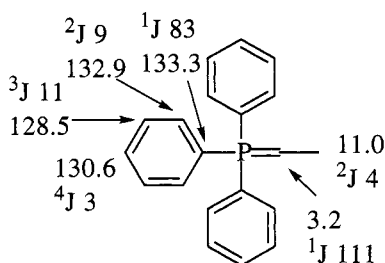


^{13}C Chemical Shifts and ^{31}P - ^{13}C Coupling Constants of Aromatic Phosphorus Compounds (δ in ppm relative to TMS, $|J|$ in Hz)



Misc.

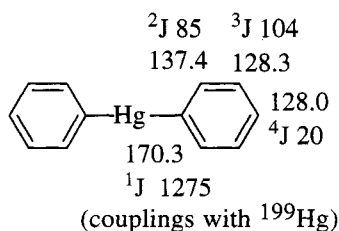
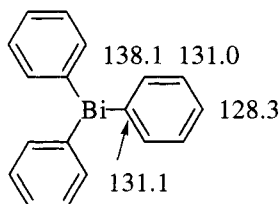
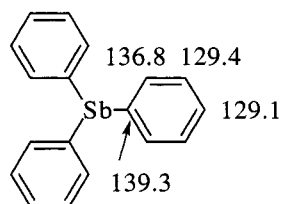
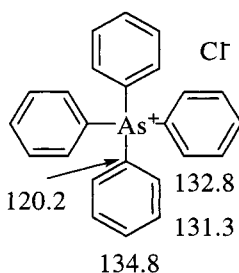
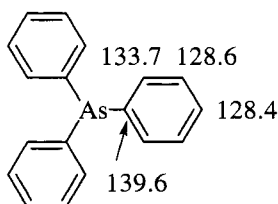
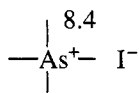
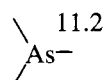
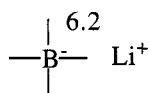
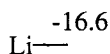
¹³C Chemical Shifts and ³¹P-¹³C Coupling Constants of Phosphoranes (δ in ppm relative to TMS, $|J|$ in Hz)



4.12.3

Miscellaneous Organometallic Compounds

¹³C Chemical Shifts and Coupling Constants of Miscellaneous Organometallics (δ in ppm relative to TMS, $|J|$ in Hz)



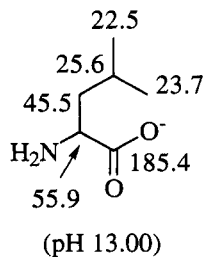
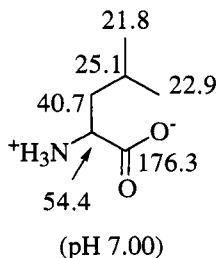
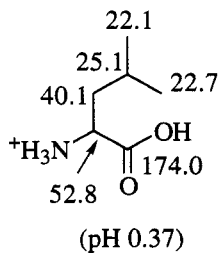
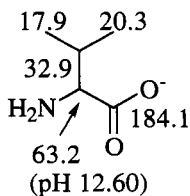
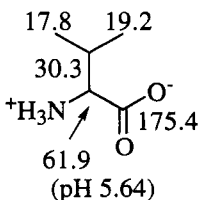
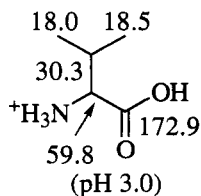
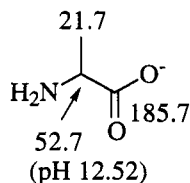
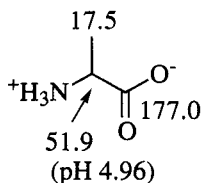
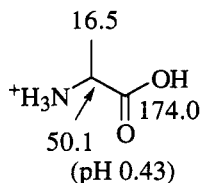
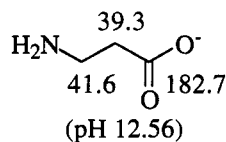
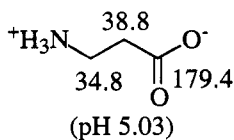
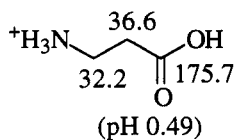
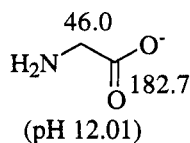
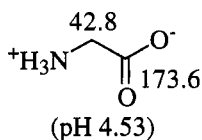
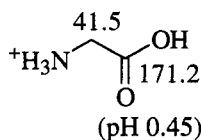
Misc.

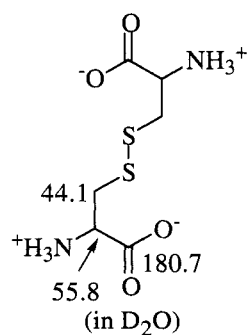
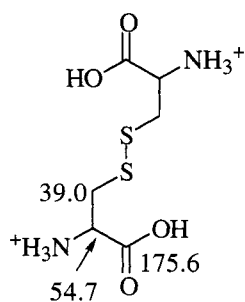
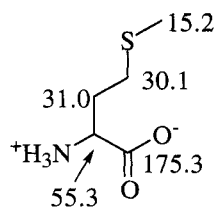
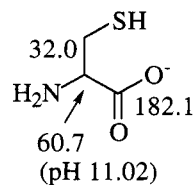
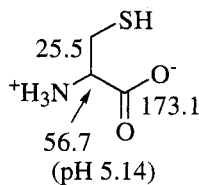
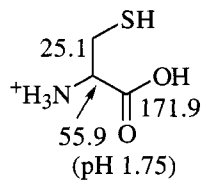
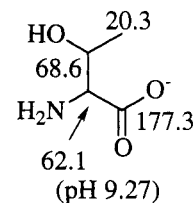
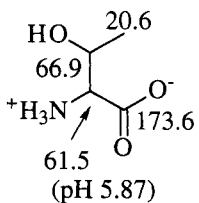
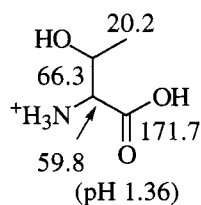
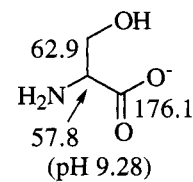
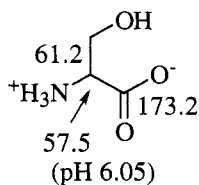
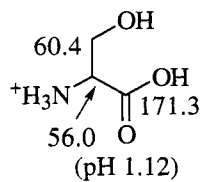
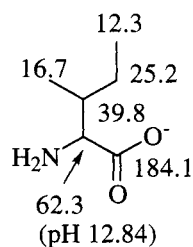
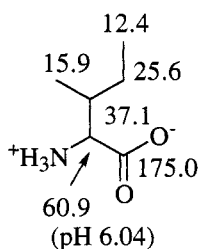
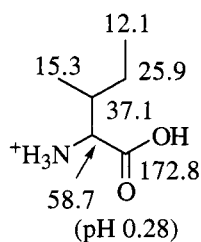
4.13

Natural Products

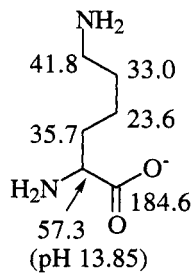
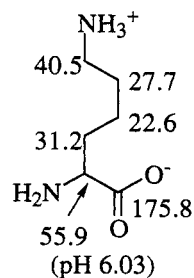
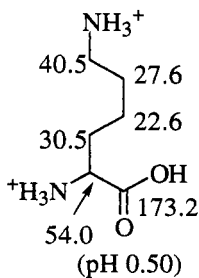
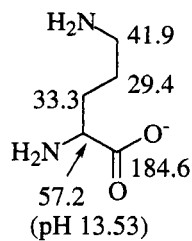
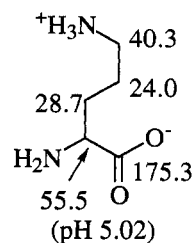
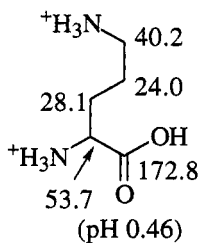
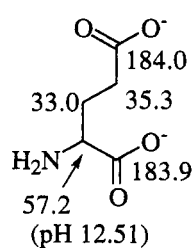
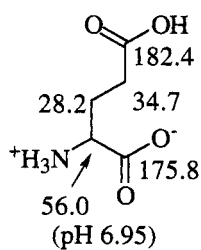
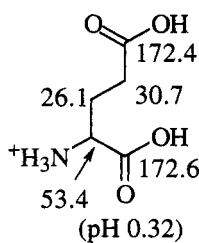
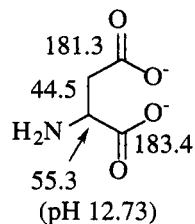
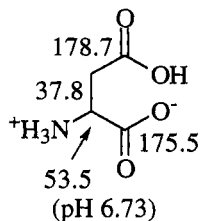
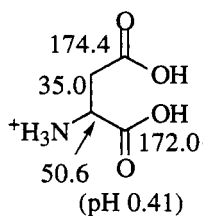
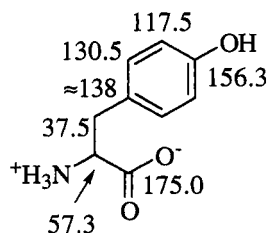
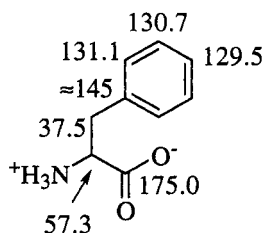
4.13.1

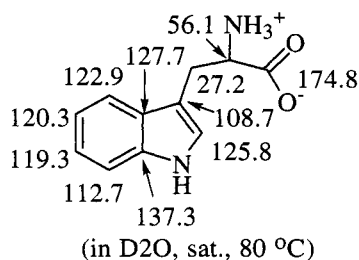
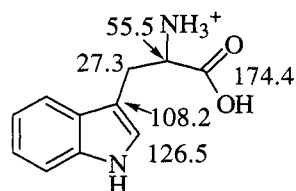
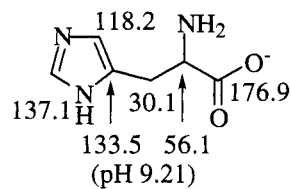
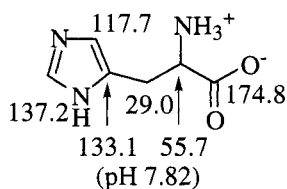
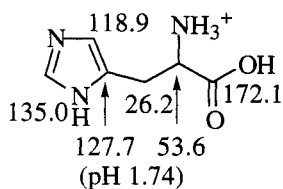
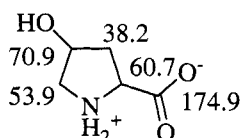
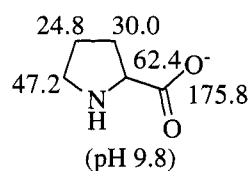
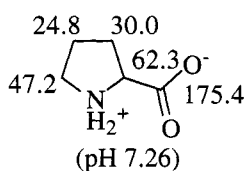
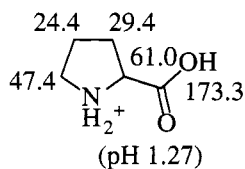
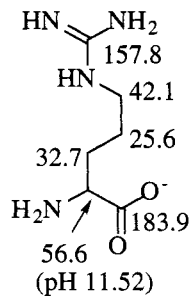
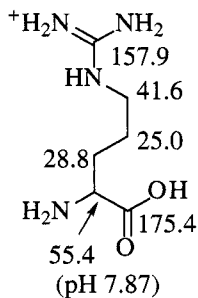
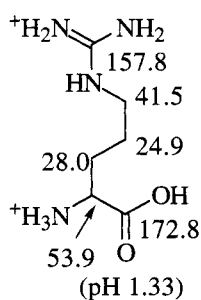
Amino Acids

 *^{13}C Chemical Shifts of Amino Acids**(δ in ppm relative to TMS; solvent: water)*Natural
Products



Natural
Products

Natural
Products

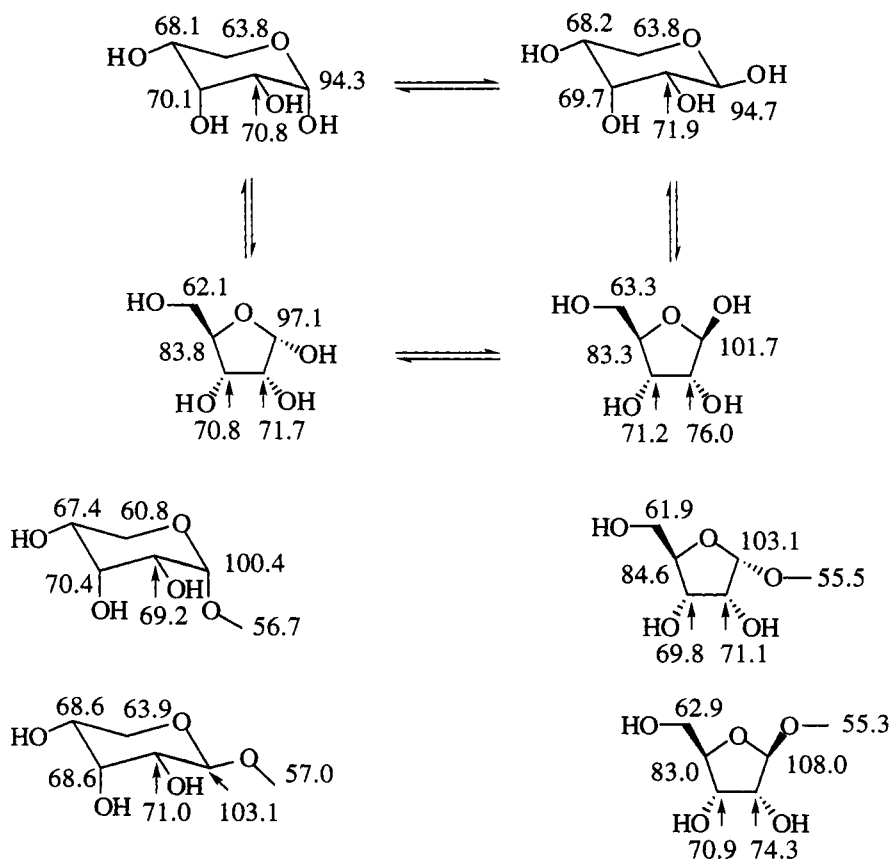


4.13.2

Carbohydrates

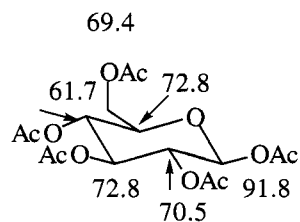
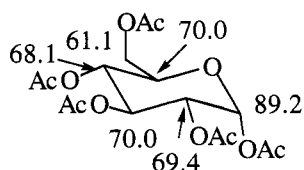
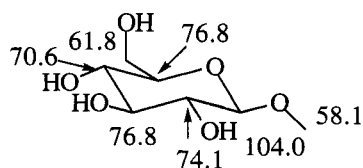
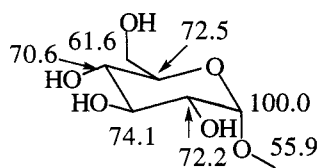
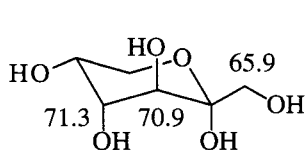
 ^{13}C Chemical Shifts of Monosaccharides(δ in ppm relative to TMS)

Ribose

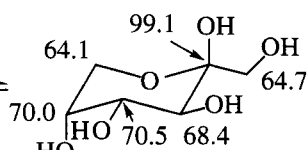


Glucose

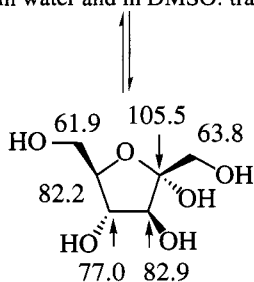
Natural
Products

*Fructose*

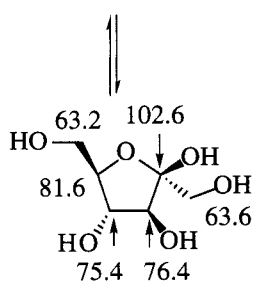
in water and in DMSO: traces



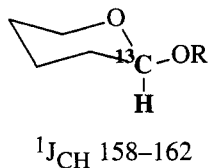
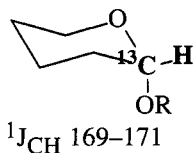
in water: 75%; in DMSO: 25%



in water: 4%; in DMSO: 20%

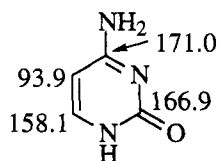


in water: 21%; in DMSO: 55%

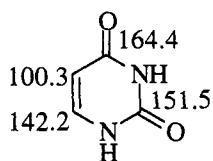
¹³C-¹H Coupling Constants through one Bond (¹J_{CH} in Hz)Natural
Products

4.13.3

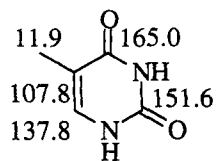
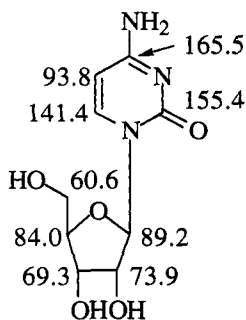
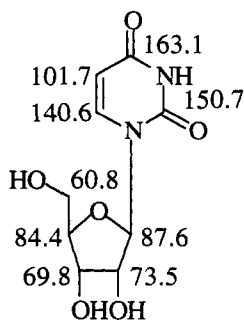
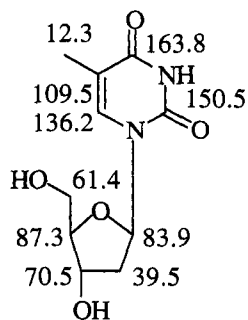
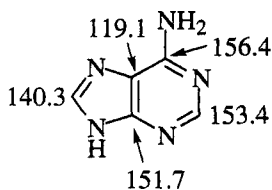
Nucleotides and Nucleosides

 *^{13}C Chemical Shifts of Nucleotides and Nucleosides**(δ in ppm relative to TMS)*

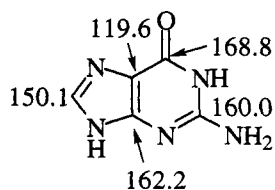
(in DMSO/water, 1:2)

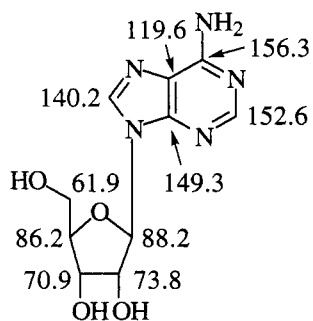


(in DMSO)

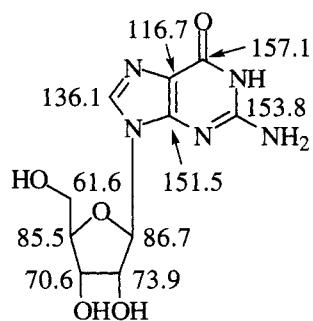
(in D_2O)(in D_2O)(in D_2O)(in D_2O)

(in DMSO)

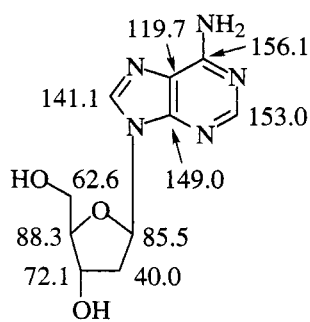
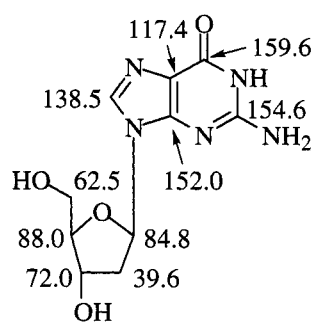
(in D_2O)



(in DMSO)

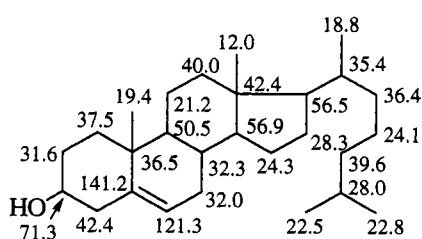
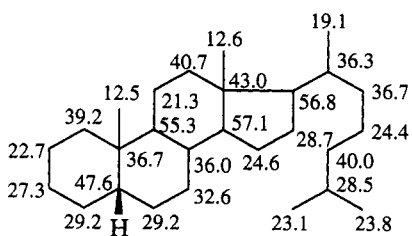
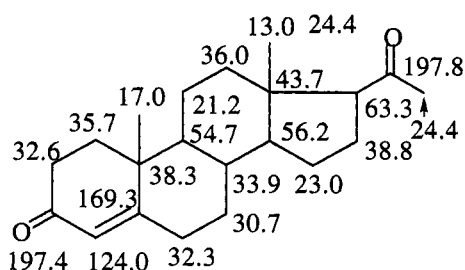
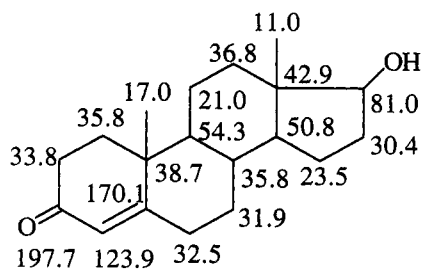
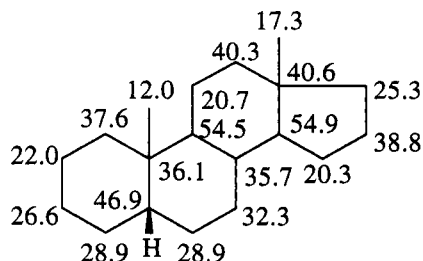
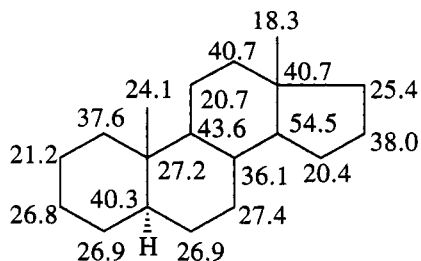


(in DMSO)

(in D₂O)(in D₂O)

4.13.4 Steroids

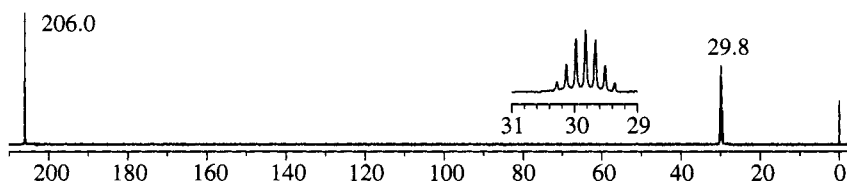
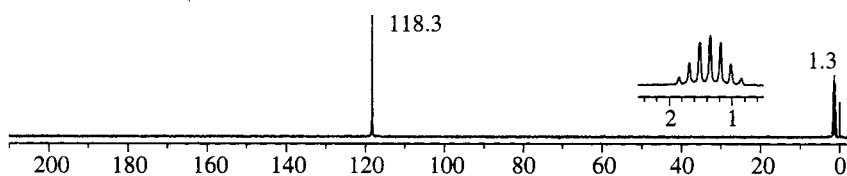
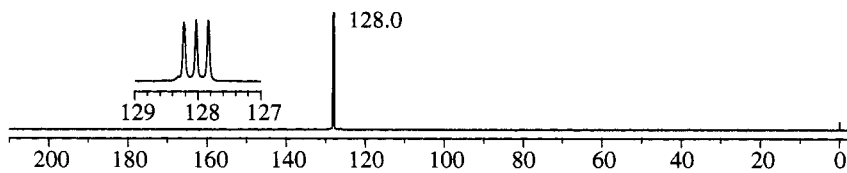
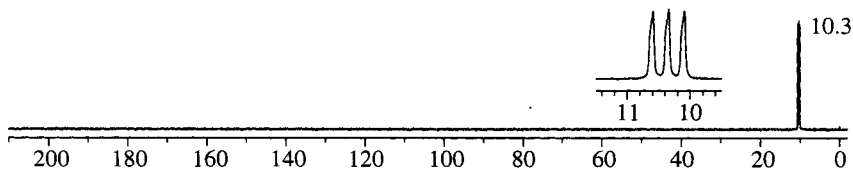
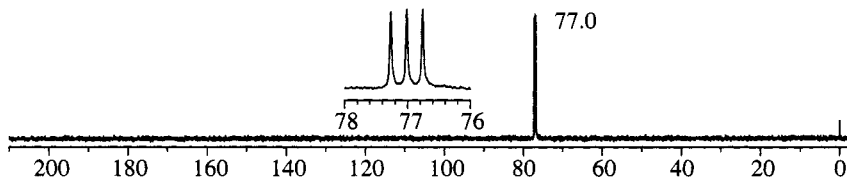
^{13}C Chemical Shifts of Steroids (δ in ppm relative to TMS)



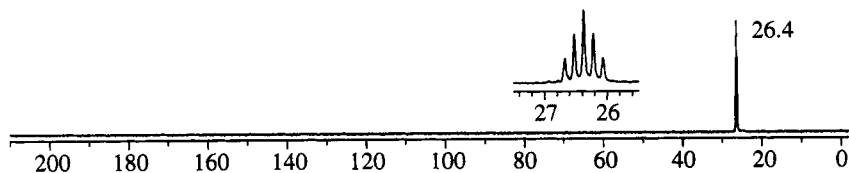
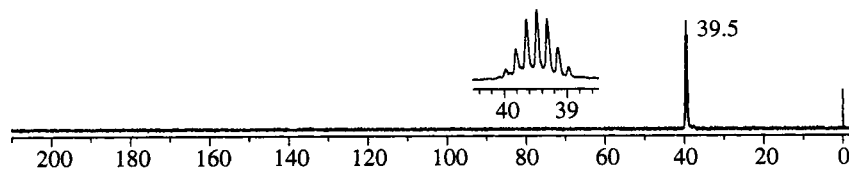
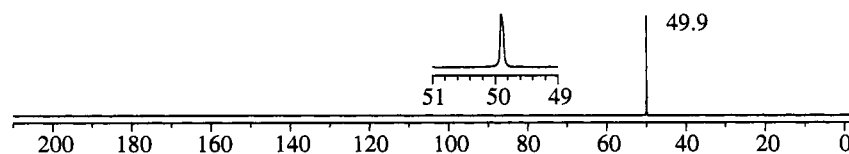
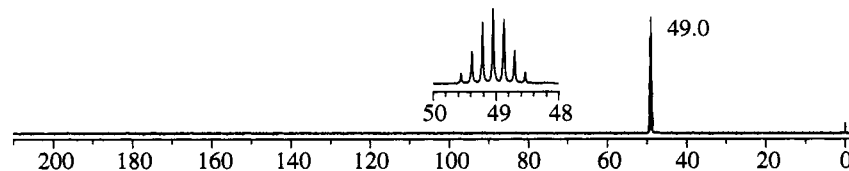
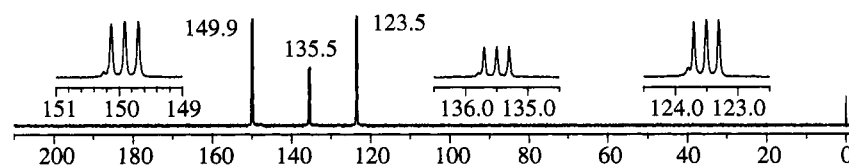
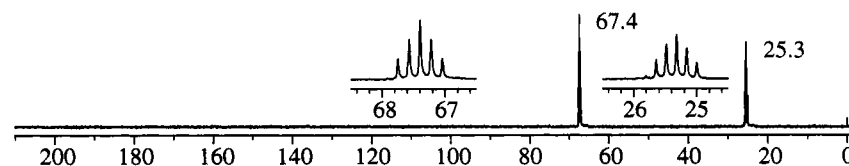
4.14

Spectra of Solvents and Reference Compounds

4.14.1

 ^{13}C NMR Spectra of Common Deuterated Solvents(125 MHz, δ in ppm relative to TMS)Acetone- d_6 Acetonitrile- d_3 Benzene- d_6 Bromoform- d Chloroform- d 

Solvents

Cyclohexane- d_{12} Dimethyl sulfoxide- d_6 Methanol- d_1 Methanol- d_4 Pyridine- d_5 Tetrahydrofuran- d_8 

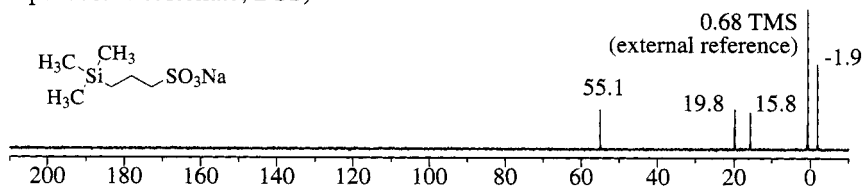
Solvents

4.14.2

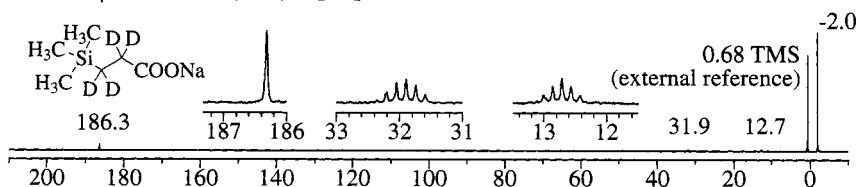
 ^{13}C NMR Spectra of Secondary Reference Compounds

Chemical shifts in ^{13}C NMR spectra are usually reported relative to the peak position of tetramethylsilane (TMS), which is added as an internal reference. When TMS is not sufficiently soluble in the sample, use of a capillary containing TMS as external reference is recommended. Owing to the different volume susceptibilities, the local magnetic fields differ in the solvent and reference. Therefore, the position of the reference must be corrected. For a D_2O solution in a cylindrical sample and TMS in a capillary, the correction amounts to +0.68 and -0.34 ppm for superconducting and electromagnets, respectively. These values must be subtracted from the shifts relative to external TMS if its position is set to 0.00 ppm. Alternatively, secondary references with $(\text{CH}_3)_3\text{SiCH}_2$ groups may be used. The following spectra of two secondary reference compounds in D_2O were measured at 125 MHz with TMS as external reference. Chemical shifts are reported in ppm relative to TMS upon correction for the difference in the volume susceptibilities of D_2O . As a result, the peak for the external TMS appears at 0.68 ppm.

3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (sodium 4,4-dimethyl-4-silapentane-1-sulfonate; DSS)



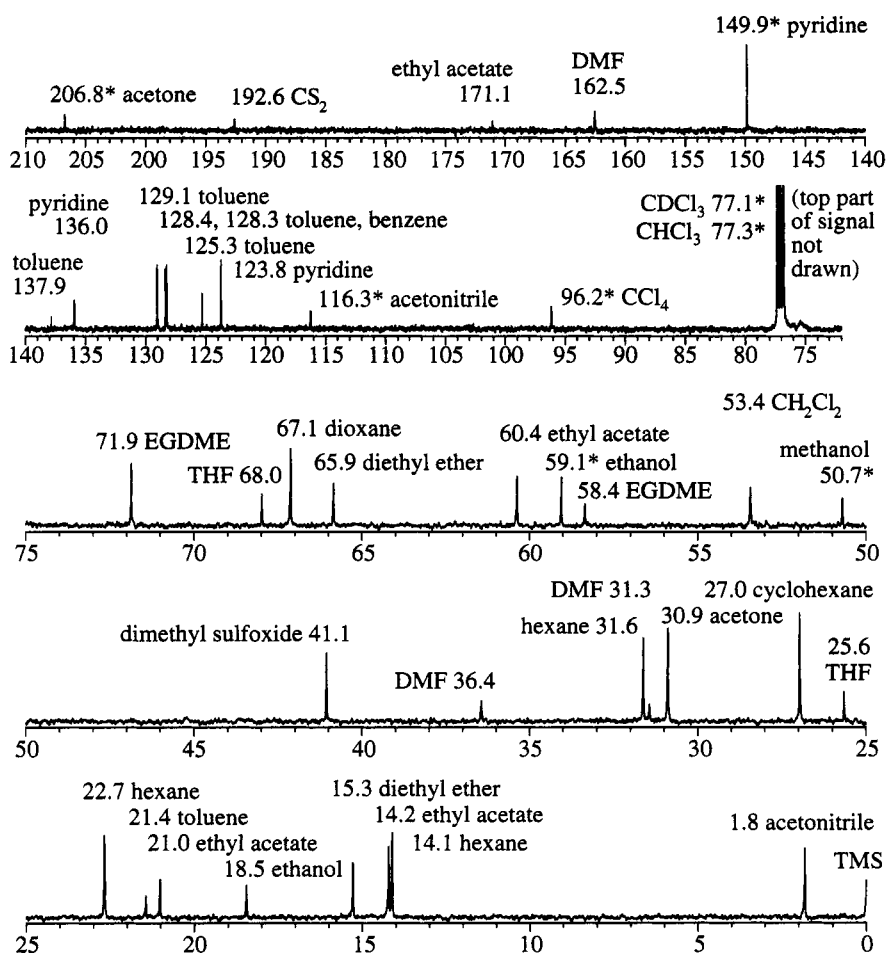
2,2,3,3- D_4 -3-(Trimethylsilyl)-propionic acid sodium salt



4.14.3

 ^{13}C NMR Spectrum of a Mixture of Common Nondeuterated Solvents

This broad band-decoupled ^{13}C NMR spectrum of a CDCl_3 sample with 20 common solvents (0.05-0.4 vol%) is shown as a guide for the identification of solvent impurities (125 MHz, δ in ppm relative to TMS). Chemical shifts of signals marked with an asterisk (*) may change up to a few ppm if the sample contains solutes with functional groups that can form hydrogen bonds. DMF: dimethyl formamide; THF: tetrahydrofuran; EGDME: ethylene glycol dimethyl ether.



Solvents

5 ^1H NMR Spectroscopy



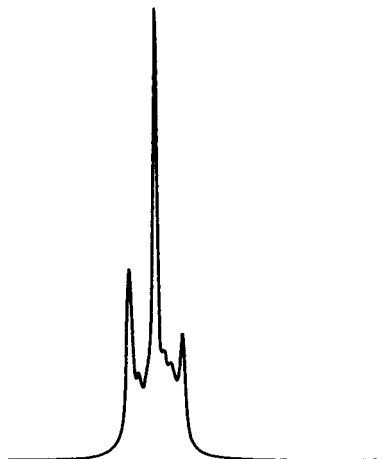
5.1 Alkanes

5.1.1 Chemical Shifts

^1H Chemical Shifts of Alkanes (δ in ppm relative to TMS, J in Hz)

CH_4 0.23	$J_{\text{gem}} -12.4$	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_3 \end{array}$ 0.86	$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH}_2 \\ \\ \text{CH}_3 \end{array}$ 0.91	$J_{\text{vic}} 7.4$
				1.33
$\begin{array}{c} \text{CH}_3 \\ \\ \text{CH} \\ / \quad \backslash \\ \text{CH}_3 \quad \text{CH}_3 \end{array}$ 0.89	$J_{\text{vic}} 6.8$	$\begin{array}{c} \text{CH}_3 \text{ a} \\ \\ \text{CH}_2 \text{ b} \\ \\ \text{CH}_2 \text{ c} \\ \\ \text{CH}_3 \end{array}$ 0.91	$^3J_{\text{ab}} 7.3$	
1.74		1.31	$^2J_{\text{bb}'} -12.4$	
			$^3J_{\text{bc}} 5.7$	
			$^3J_{\text{bc}'} 8.5$	

In long-chain alkanes, the methyl groups at ca. 0.8 ppm typically show distorted triplets because of second order effects:





^1H Chemical Shifts of Monosubstituted Alkanes
(δ in ppm relative to TMS)

Substituent	Methyl	Ethyl		Propyl			
	-CH ₃	-CH ₂	-CH ₃	-CH ₂	-CH ₃		
C	-H	0.23	0.86	0.86	0.91	1.33	0.91
	-CH=CH ₂	1.71	2.00	1.00	2.02	1.43	0.91
	-C≡CH	1.80	2.16	1.15	2.10	1.50	0.97
H a l	-phenyl	2.35	2.63	1.21	2.59	1.65	0.95
	-F	4.27	4.36	1.24	4.30	1.68	0.97
	-Cl	3.06	3.47	1.33	3.47	1.81	1.06
	-Br	2.69	3.37	1.66	3.35	1.89	1.06
O	-I	2.16	3.16	1.88	3.16	1.88	1.03
	-OH	3.39	3.59	1.18	3.49	1.53	0.93
	-O-alkyl	3.24	3.37	1.15	3.27	1.55	0.93
	-OCH=CH ₂	3.16	3.66	1.21			
N	-O-phenyl	3.73	3.98	1.38	3.86	1.70	1.05
	-OCOCH ₃	3.67	4.12	1.26	4.02	1.65	0.95
	-OCO-phenyl	3.88	4.37	1.38	4.25	1.76	1.07
	-OSO ₂ -4-tolyl	3.70	4.07	1.30	3.94	1.60	0.95
	-NH ₂	2.47	2.74	1.10	2.61	1.43	0.93
	-NHCH ₃	2.3					
	-N(CH ₃) ₂	2.31	2.32	1.06			
S	-NHCOCH ₃	2.79	3.26	1.14	3.18	1.55	0.96
	-NO ₂	4.29	4.37	1.58	4.28	2.01	1.03
	-CN	1.98	2.35	1.31	2.29	1.71	1.11
	-NC	2.85	3.39	1.28			
	-SH	2.00	2.44	1.31	2.50	1.63	0.99
	-S-alkyl	2.09	2.49	1.25	2.43	1.59	0.98
	-SS-alkyl	2.30	2.67	1.35	2.63	1.71	1.03
O C / \	-SOCH ₃	2.50					
	-SO ₂ CH ₃	2.84	2.94	2.80			
	-CHO	2.20	2.46	1.13	2.42	1.67	0.97
	-COCH ₃	2.09	2.47	1.05	2.32	1.56	0.93
	-CO-phenyl	2.55	2.92	1.18	2.86	1.72	1.02
	-COOH	2.10	2.36	1.16	2.31	1.68	1.00
	-COOCH ₃	2.01	2.32	1.15	2.22	1.65	0.98
	-CONH ₂	2.02	2.23	1.13	2.19	1.68	0.99
	-COCl	2.66	2.93	1.24	2.87	1.74	1.00

¹H Chemical Shifts of Monosubstituted Alkanes (contd.)
 (δ in ppm relative to TMS)



Substituent	Isopropyl		Butyl				tert-Butyl
	-CH	-CH ₃	-CH ₂	-CH ₂	-CH ₂	-CH ₃	-CH ₃
-H	1.33	0.91	0.91	1.31	1.31	0.91	0.89
C -CH=CH ₂			2.06	≈1.5	≈1.2	0.90	1.02
-C≡CH	2.59	1.15	2.18	1.52	1.41	0.92	1.22
-phenyl	2.89	1.25	2.61	1.60	1.34	0.93	1.32
H -F			4.34	1.65		0.95	1.34
a -Cl	4.14	1.55	3.42	1.68	1.41	0.92	1.60
i -Br	4.21	1.73					1.76
-I	4.24	1.89	3.20	1.80	1.42	0.93	1.95
-OH	3.94	1.16	3.63	1.53	1.39	0.94	1.22
-O-alkyl	3.55	1.08	3.40	1.54	1.38	0.92	1.24
-OCH=CH ₂	4.06	1.23	3.68	1.61	1.39	0.94	
-O-phenyl	4.51	1.31	3.94	1.76	1.47	0.97	
-OCOCH ₃	4.99	1.23	4.06	1.60	1.39	0.94	1.45
-OCO-phenyl	5.22	1.37					1.58
-OSO ₂ -4-tolyl	4.70	1.25	4.03	1.62	1.36	0.88	
N -NH ₂	3.07	1.03	2.68	1.43	1.33	0.92	1.15
-NHCOCH ₃	4.01	1.13	3.21	1.49	1.35	0.92	1.28
-NO ₂	4.44	1.53	4.47	2.07	1.50	1.07	1.59
-CN	2.67	1.35	2.34	1.63	1.50	0.96	1.37
-NC	3.87	1.45					1.44
S -SH	3.16	1.34	2.52	1.59	1.43	0.92	1.43
-S-alkyl	2.93	1.25	2.49	1.56	1.42	0.92	1.39
-SS-alkyl			2.69	1.64	1.42	0.93	1.32
-SO ₂ CH ₃	3.13	1.41					1.44
O -CHO	2.39	1.13	2.42	1.59	1.35	0.93	1.07
 -COCH ₃	2.54	1.08					1.12
C -CO-phenyl	3.58	1.22	2.95	1.72	1.41	0.96	
/ \ -COOH	2.56	1.21	2.35	1.62	1.39	0.93	1.23
-COOCH ₃	2.56	1.17	2.31	1.61	1.33	0.92	1.20
-CONH ₂	2.44	1.18	2.22	1.60	1.37	0.93	1.22
-COCl	2.97	1.31	2.88	1.67	1.40	0.93	



Estimation of ^1H Chemical Shifts of Aliphatic Compounds
 (δ in ppm relative to TMS) [1]

$$\text{CH}_3 \quad \delta_{\text{CH}_3\text{X}} = 0.86 + Z_\alpha$$

$$\delta_{\text{CH}_3\text{CXYZ}} = 0.86 + \sum_i Z_{\beta_i}$$

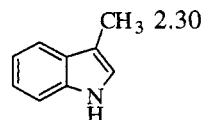
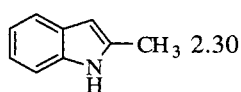
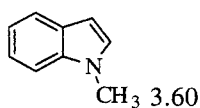
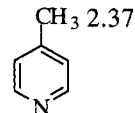
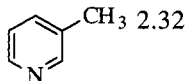
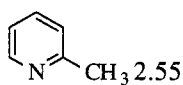
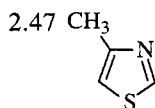
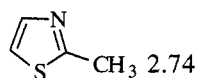
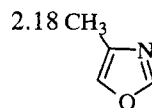
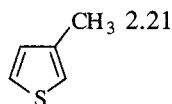
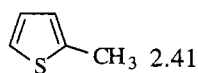
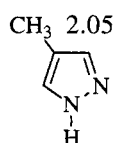
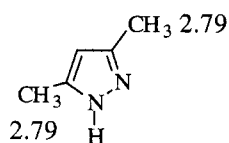
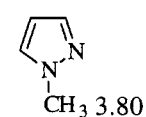
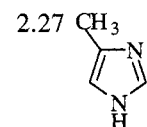
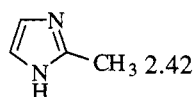
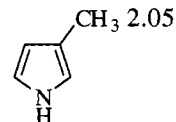
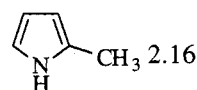
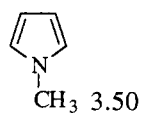
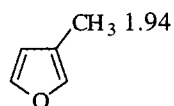
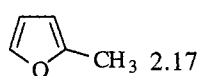
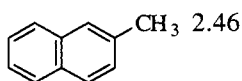
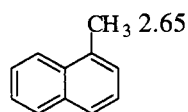
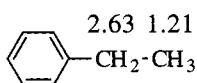
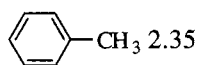
$$\text{CH}_2 \quad \delta_{\text{CH}_2} = 1.37 + \sum_i Z_{\alpha_i} + \sum_j Z_{\beta_j}$$

$$\text{CH} \quad \delta_{\text{CH}} = 1.50 + \sum_i Z_{\alpha_i} + \sum_j Z_{\beta_j}$$

Substituent (X, Y, Z)		CH_3		CH_2		CH	
		Z_α	Z_β	Z_α	Z_β	Z_α	Z_β
	-C	0.00	0.05	0.00	-0.04	0.17	-0.01
	-C=C	0.85	0.20	0.63	0.00	0.68	0.03
	-C \equiv C-	0.94	0.32	0.70	0.13	1.04	
	-phenyl	1.49	0.38	1.22	0.29	1.28	0.38
H a l	-F	3.41	0.41	2.76	0.16	1.83	0.27
	-Cl	2.20	0.63	2.05	0.24	1.98	0.31
	-Br	1.83	0.83	1.97	0.46	1.94	0.41
	-I	1.30	1.02	1.80	0.53	2.02	0.15
O	-OH	2.53	0.25	2.20	0.15	1.73	0.08
	-O-C	2.38	0.25	2.04	0.13	1.35	0.32
	-OC=C	2.64	0.36	2.63	0.33		
	-O-phenyl	2.87	0.47	2.61	0.38	2.20	0.50
	-O(C=O)-	2.81	0.44	2.83	0.24	2.47	0.59
N	-N	1.61	0.14	1.32	0.22	1.13	0.23
	-N ⁺	2.44	0.39	1.91	0.40	1.78	0.56
	-N(C=O)-	1.88	0.34	1.63	0.22	2.10	0.62
	-NO ₂	3.43	0.65	3.08	0.58	2.31	
	-CN	1.12	0.45	1.08	0.33	1.00	
	-NCS	2.51	0.54	2.27		2.14	
S	-S-	1.14	0.45	1.23	0.26	1.06	0.31
	-SCO-	1.41	0.37	1.54	0.63	1.31	0.19
	-S(=O)-	1.64	0.36			1.25	
	-S(=O) ₂ -	1.98	0.42	2.08	0.52	1.50	
	-SCN	1.75	0.66	1.62		1.64	
O 	-CHO	1.34	0.21	1.07	0.29	0.86	0.22
	-CO-	1.23	0.20	1.12	0.24		
C	-COOH	1.22	0.23	0.90	0.23	0.87	0.32
	-COO-	1.15	0.28	0.92	0.35	0.83	0.63
/ \	-CO-N	1.16	0.28			0.94	
	-COCl	1.94		1.51			

For other approaches: see [2]

¹H Chemical Shifts of Aromatically Substituted Alkanes
 (δ in ppm relative to TMS)





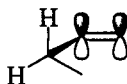
5.1.2 Coupling Constants



Geminal Coupling Constants ($^2J_{\text{HH}}$ in Hz)



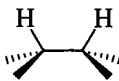
$^2J_{\text{HCH}}$ -8 to -18 Hz

Electronegative substituents cause a decrease in $|J|_{\text{gem}}$, while a double or triple bond next to the CH_2 group causes an increase. The latter effect is strongest if one of the C-H bonds is parallel to the π orbitals:



Compound	J_{gem}	Compound	J_{gem}
CH_4	-12.4	CH_3COCH_3	-14.9
CH_3Cl	-10.8	CH_3COOH	-14.5
CH_2Cl_2	-7.5	CH_3CN	-16.9
CH_3OH	-10.8	$\text{CH}_2(\text{CN})_2$	-20.3
 - CH_3	-14.3	 - CH_2 -CN	-18.5

Vicinal Coupling Constants ($^3J_{\text{HH}}$ in Hz)



conformation not fixed: $^3J_{\text{HH}} \approx 7$

fixed: $^3J_{\text{HH}} \approx 0 - 18$

Influence of Substituents on the Vicinal Coupling Constant

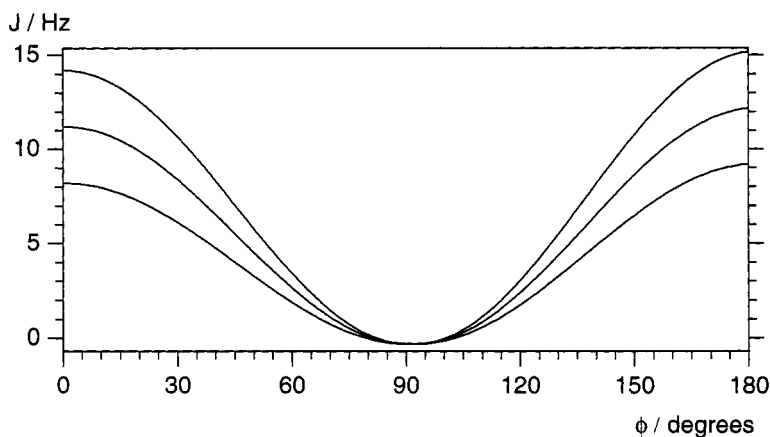
Compound	J_{vic}	Compound	J_{vic}	Compound	J_{vic}
$\text{CH}_3\text{CH}-\text{F}_2$	4.5	$\text{CH}_3\text{CH}_2-\text{OH}$	6.9	$\text{CH}_3\text{CH}_2-\text{CN}$	7.6
$\text{CH}_3\text{CH}-\text{Cl}_2$	6.1	$(\text{CH}_3\text{CH}_2)_3\text{O}^+\text{BF}_4^-$	7.2	$(\text{CH}_3\text{CH}_2)_2\text{S}$	7.4
$\text{CH}_3\text{CH}_2-\text{F}$	6.9	$(\text{CH}_3\text{CH}_2)_3\text{N}$	7.1	$\text{CH}_3\text{CH}_2-\text{Li}$	8.4
$\text{CH}_3\text{CH}_2-\text{Cl}$	7.2				

Vicinal coupling constants strongly depend on the dihedral angle, ϕ (Karplus equation):



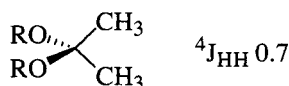
$$\begin{aligned} J &= J^0 \cos^2 \phi - 0.3 & 0^\circ \leq \phi \leq 90^\circ \\ J &= J^{180} \cos^2 \phi - 0.3 & 90^\circ \leq \phi \leq 180^\circ \end{aligned}$$

The same relationship between torsional angle and vicinal coupling constant holds for substituted alkanes if appropriate values are used for J^0 and J^{180} . These limiting values depend on the electronegativity and orientation of substituents, the hybridization of carbon atoms, bond lengths, and bond angles.



Long-Range Coupling Constants ($|J|_{HH}$ in Hz)

Coupling constants through more than three bonds (long-range coupling) in alkanes are generally much smaller than 1 Hz and thus not visible in routine 1D NMR spectra. They are, however, much larger than 1 Hz for fixed conformations (e.g. in condensed alicyclic systems, see Chapter 5.4) and in unsaturated compounds (see Chapter 5.2). They are also significant when electronegative substituents are present between the coupling partners, as e.g.:



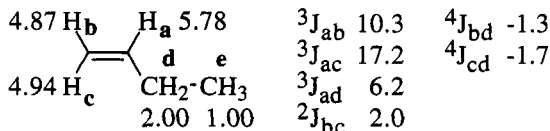
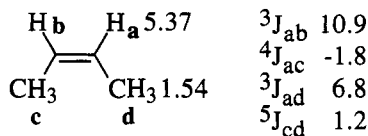
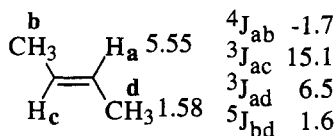
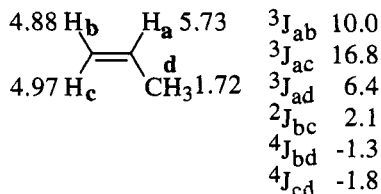
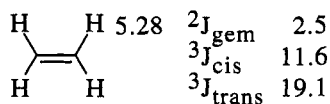
5.1.3 References

- [1] R. Bürgin Schaller, C. Arnold, E. Pretsch, New parameters for predicting ^1H NMR chemical shifts of protons attached to carbon atoms, *Anal. Chim. Acta* **1995**, 312, 95.
- [2] E. Friedrich, K.G. Runkle, Empirical NMR chemical shift correlations for methyl and methylene protons, *J. Chem. Educ.* **1984**, 61, 830.

5.2 Alkenes

$\text{C}=\text{C}$ 5.2.1 Substituted Ethylenes

^1H NMR Chemical Shifts and Coupling Constants of Alkenes (δ in ppm relative to TMS, J in Hz)



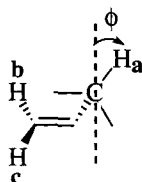
Geminal and Vicinal Coupling of Alkenes (J in Hz)

The coupling constants strongly depend on the electronegativity of the substituents (see Table on pp 170, 171). They decrease with increasing electronegativity and number of electronegative substituents. The same trend holds for the signed values of *geminal* coupling constants but not for the absolute values because J_{gem} can be positive or negative. Although the total ranges of *cis* and *trans* vicinal coupling constants overlap, $J_{\text{trans}} > J_{\text{cis}}$ always holds for given substituents.

Typical ranges:	J_{gem}	-4 to 4
	J_{cis}	4 to 12
	J_{trans}	14 to 19

Coupling Over More than Three Bonds in Alkenes (Long-Range Coupling) (J in Hz)

Allylic Coupling



$$\text{cisoid: } J_{ab} \text{ } -3.0 \text{ to } +2.0$$

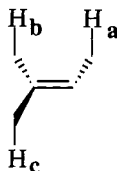
$$\text{transoid: } J_{ac} \text{ } -3.5 \text{ to } +2.5$$



In acyclic systems, $|J|_{\text{cisoid}} > |J|_{\text{transoid}}$ usually holds. The magnitudes of the coupling constants depend on the conformation. Largest absolute values are observed if the C-H bond of the substituents overlaps with the π -electrons ($\phi = 0$):

ϕ	J_{ab}	J_{ac}
0°	-3.0	-3.5
90°	+1.8	+2.2
180°	-3.0	-3.5
270°	0.0	0.8

Homoallylic Coupling

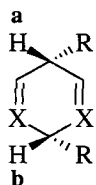


$$\text{cisoid: } |J|_{ab} \text{ } 0-3$$

$$\text{transoid: } |J|_{ac} \text{ } 0-3$$

Allylic and homoallylic couplings with methyl groups are often comparable:
 $^4J_{\text{H-C}=\text{C}-\text{CH}_3} \approx ^5J_{\text{CH}_3-\text{C}=\text{C}-\text{CH}_3}$

In acyclic systems, $|J|_{\text{cisoid}} < |J|_{\text{transoid}}$ usually holds. Large homoallylic coupling constants are generally observed in cyclic systems:



$$J_{ab} \text{ } 5-11$$

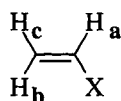


$$J_{ab} \text{ } 0-7$$

X: O, NH
 R: any substituent

X: CH, N
 R: any substituent

^1H Chemical Shifts and Coupling Constants of Monosubstituted Ethylenes (δ in ppm relative to TMS, J in Hz)



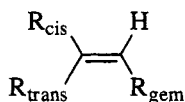
Substituent X	H_a	H_b	H_c	J_{ab}	J_{ac}	J_{bc}	Other
-H	5.28	5.28	5.28	19.1	11.6	2.5	
C -CH ₃	5.73	4.97	4.88	16.8	10.0	2.1	CH ₃ 1.72
-CH ₂ CH=CH ₂	5.71	4.95	4.92	16.9	10.3	2.2	CH ₂ 2.72
-CH ₂ -phenyl	5.89	5.01	5.00	17.0	10.0	1.9	CH ₂ 3.19
-cyclopropyl	5.32	5.04	4.84	17.1	10.4	1.8	
-cyclohexyl	5.79	4.95	4.88	17.6	10.5	1.9	
-CH ₂ F	5.89	5.24	5.12	17.2	10.6	1.5	CH ₂ 4.69
-CF ₃	5.90	5.85	5.56	17.5	11.1	0.2	
-CH ₂ Cl	5.93	5.30	5.17	16.9	10.1	1.3	CH ₂ 3.91
-CH ₂ Br	5.99	5.29	5.11	16.8	10.0	1.2	CH ₂ 3.87
-CH ₂ I	6.04	5.23	5.95	16.5	9.7	1.3	CH ₂ 3.82
-CH ₂ OH	5.98	5.26	5.12	17.4	10.5	1.7	CH ₂ 4.12
-CH ₂ NH ₂	5.97	5.15	5.04	17.3	10.4	1.7	CH ₂ 3.29
-CH ₂ NO ₂	6.11	5.46	5.49	16.7	10.7	0.8	CH ₂ 4.93
-CH=C=CH ₂	6.31	5.19	4.99	17.2	10.1	1.6	
-C \equiv C-CH ₃	5.62	5.39	5.24	17.0	11.1	2.3	
-phenyl	6.72	5.72	5.20	17.9	11.1	1.0	
-2-naphthyl	6.87	5.86	5.32				
-2- <i>m</i> -xylyl	6.65	5.22	5.48	17.9	11.4	2.1	CH ₃ 2.27
-2-nitrophenyl	7.19	5.68	5.45	17.4	10.7	1.1	
-3-nitrophenyl	6.74	5.86	5.42	17.5	10.9	0.4	
-4-nitrophenyl	6.77	5.90	5.48	17.4	10.9	0.8	
-2-pyridyl	6.84	6.22	5.45	18.5	11.3	1.4	
-4-pyridyl	6.61	5.91	5.42	17.6	10.8	0.7	
H -F	6.17	4.37	4.03	12.8	4.7	-3.2	
a -Cl	6.26	5.48	5.39	14.5	7.5	-1.4	
I -Br	6.44	5.84	5.97	14.9	7.1	-1.9	
-I	6.53	6.57	6.23	15.9	7.8	-1.5	
O -OH	6.45	4.18	3.82				
-OCH ₃	6.44	4.03	3.88	14.1	7.0	-2.0	CH ₃ 3.16
-OCH ₂ CH ₃	6.46	4.17	3.96	14.4	6.9	-1.9	
-OCH=CH ₂	6.49	4.52	4.21	14.0	6.4	-1.8	
-O-phenyl	6.64	4.74	4.40	13.7	6.1	-1.6	
-OCHO	7.33	4.96	4.66	13.9	6.4	-1.7	CHO 8.07
-OCOCH ₃	7.28	4.88	4.56	14.1	6.3	-1.6	CH ₃ 2.13
-OCOCH=CH ₂	7.39	4.96	4.62	14.2	6.4	-1.6	
-OCO-phenyl	7.52	5.04	4.67	13.8	6.3	-1.7	
-OPO(OCH ₂ CH ₃) ₂	6.58	4.91	4.59	13.8	6.0	-2.1	

Substituent X	H _a	H _b	H _c	J _{ab}	J _{ac}	J _{bc}	Other
N -NH ₂	≈6.05	≈4.04	≈3.99				
-N ⁺ (CH ₃) ₃ Br ⁻	6.50	5.76	5.54	15.1	8.2	-4.3	
-NHCOCH ₃	≈7.33	≈4.53	≈4.68				
-NO ₂	7.12	6.55	5.87	14.6	7.0	1.4	
-CN	5.73	6.20	6.07	17.9	11.8	0.9	
-NC	5.90	5.58	5.35	15.6	8.6	-0.5	
-NCO	6.12	5.01	4.77	15.2	7.6	-0.1	
S -SCH ₃	6.35	4.84	5.08	16.4	10.3	-0.3	CH ₃ 2.12
-S-phenyl	6.53	5.32	5.32	16.7	9.6	-0.2	
-S(O)CH ₃	6.77	6.08	5.92	16.7	9.8	-0.6	CH ₃ 2.61
-SO ₂ CH ₃	6.76	6.43	6.14	16.5	10.0	-0.5	CH ₃ 2.96
-SO ₂ CH=CH ₂	6.67	6.41	6.17	16.4	10.0	-0.6	
-SO ₂ OH	6.73	6.41	6.13	16.8	10.2	-1.2	
-SO ₂ OCH ₃	6.57	6.43	6.22	16.9	10.1	-0.6	CH ₃ 3.85
-SO ₂ NH ₂	6.93	6.17	5.98	16.3	10.0	0.0	NH ₂ 6.7
-SO ₂ NH-phenyl	6.56	6.18	5.86	16.7	10.1	-0.3	NH 9.07
-SF ₅	6.63	5.96	5.64	16.6	9.8	0.4	
-SCN	6.19	5.66	5.70				
O -CHO	6.26	6.11	6.26	17.4	10.0	1.0	CHO 9.51
-COCH ₃	6.30	6.27	5.90	18.7	10.7	1.3	CH ₃ 2.25
C -COCH=CH ₂	6.67	6.28	5.82	17.9	11.0	1.4	
/\ -CO-phenyl	7.20	6.52	5.81	17.7	9.9	2.3	
-COOH	6.15	6.53	5.95	17.2	10.5	1.8	COOH 12.08
-COOCH ₃	6.14	6.40	5.83	17.4	10.6	1.5	CH ₃ 3.76
-CONH ₂	6.48	6.17	5.71	17.3	7.9	5.0	NH ₂ 7.55
-CON(CH ₃) ₂	6.64	6.12	5.55	17.0	9.8	3.4	
-COF	6.14	6.60	6.25	17.3	10.7	0.8	
-COCl	6.35	6.63	6.16	17.4	10.6	0.2	
P -P(CH ₃) ₂	6.23	5.39	5.51	18.3	11.8	2.0	CH ₃ 0.95
-P(CH=CH ₂) ₂	6.16	5.59	5.64	18.4	11.8	2.0	
-PCl ₂	7.48	6.64	6.68	18.6	11.7	0.4	
-PO(phenyl) ₂	6.72	6.25	6.21	18.9	12.9	1.8	
-PSCl ₂	6.42	6.13	5.90	17.5	11.0	0.3	
-PS(CH ₃) ₂	6.60	6.26	6.14	17.9	11.8	1.8	
-PS(phenyl) ₂	6.82	6.34	6.17	17.9	11.7	1.6	
-Li				23.9	19.3	7.1	
-MgCl	6.68	5.57	6.20	23.0	17.6	7.5	
-MgBr	6.67	5.51	6.15	23.3	17.7	7.6	
-Si(CH ₃) ₃	6.11	5.63	5.88	20.2	14.6	3.8	CH ₃ 0.06
-Sn(CH=CH ₂) ₃	6.39	5.75	6.21	20.7	13.4	3.1	
-Pb(CH=CH ₂) ₃	6.70	5.46	6.19	19.8	12.2	2.1	
-HgBr	6.45	5.52	5.92	18.7	11.9	3.1	

C≡C

Estimation of ^1H Chemical Shifts of Substituted Ethylenes
(δ in ppm relative to TMS)

$\text{C} = \text{C}$



$$\delta_{\text{C}=\text{CH}} = 5.25 + Z_{\text{gem}} + Z_{\text{cis}} + Z_{\text{trans}}$$

Substituent R	Z_{gem}	Z_{cis}	Z_{trans}
-H	0.00	0.00	0.00
C -alkyl	0.45	-0.22	-0.28
-alkyl ring ¹	0.69	-0.25	-0.28
-CH ₂ -aromatic	1.05	-0.29	-0.32
-CH ₂ X, X: F, Cl, Br	0.70	0.11	-0.04
-CHF ₂	0.66	0.32	0.21
-CF ₃	0.66	0.61	0.32
-CH ₂ O	0.64	-0.01	-0.02
-CH ₂ N	0.58	-0.10	-0.08
-CH ₂ CN	0.69	-0.08	-0.06
-CH ₂ S	0.71	-0.13	-0.22
-CH ₂ CO	0.69	-0.08	-0.06
-C \equiv C	1.00	-0.09	-0.23
-C=C conjugated ²	1.24	0.02	-0.05
-C \equiv C	0.47	0.38	0.12
-aromatic	1.38	0.36	-0.07
-aromatic, fixed ³	1.60		-0.05
-aromatic, <i>o</i> -substituted	1.65	0.19	0.09
H -F	1.54	-0.40	-1.02
a -Cl	1.08	0.18	0.13
I -Br	1.07	0.45	0.55
-I	1.14	0.81	0.88
O -OC (sp^3)	1.22	-1.07	-1.21
-OC (sp^2)	1.21	-0.60	-1.00
-OCO-	2.11	-0.35	-0.64
-OPO(OCH ₂ CH ₃) ₂	1.33	-0.34	-0.66
N -NR ₂ ; R: H, C (sp^3)	0.80	-1.26	-1.21
-NR-; R: C (sp^2)	1.17	-0.53	-0.99
-NCO-R	2.08	-0.57	-0.72
-N=N-phenyl	2.39	1.11	0.67
-NO ₂	1.87	1.30	0.62
-CN	0.27	0.75	0.55

Substituent R	Z_{gem}	Z_{cis}	Z_{trans}
S -S-	1.11	-0.29	-0.13
-SO-	1.27	0.67	0.41
-SO ₂ -	1.55	1.16	0.93
-SCO-	1.41	0.06	0.02
-SCN	0.94	0.45	0.41
-SF ₅	1.68	0.61	0.49
O -CHO	1.02	0.95	1.17
 -CO-	1.10	1.12	0.87
C -CO- conjugated ²	1.06	0.91	0.74
/\ -COOH	0.97	1.41	0.71
-COOH conjugated ²	0.80	0.98	0.32
-COOR	0.80	1.18	0.55
-COOR conjugated ²	0.78	1.01	0.46
-CON	1.37	0.98	0.46
-COCl	1.11	1.46	1.01
-PO(OCH ₂ CH ₃) ₂	0.66	0.88	0.67

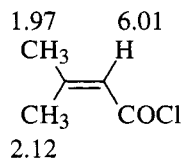
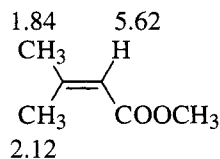
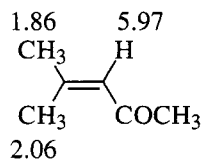
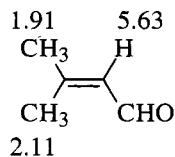
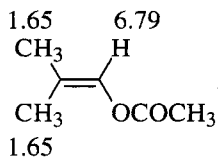
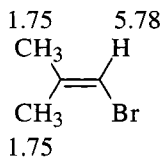
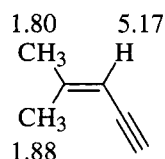
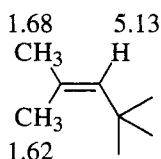
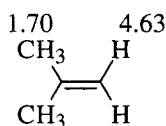
C≡C

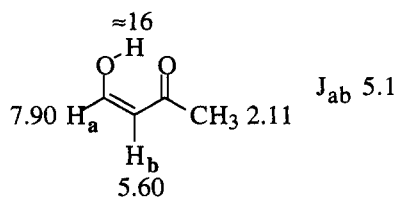
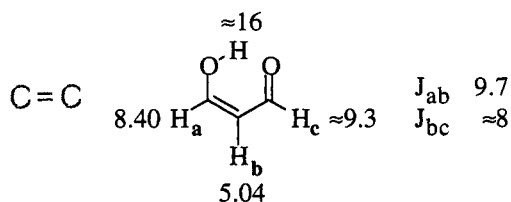
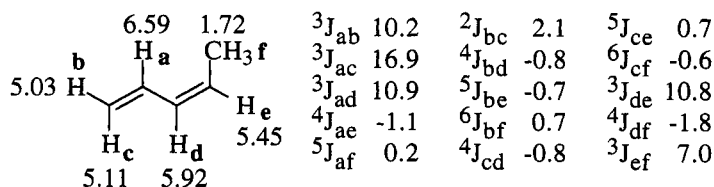
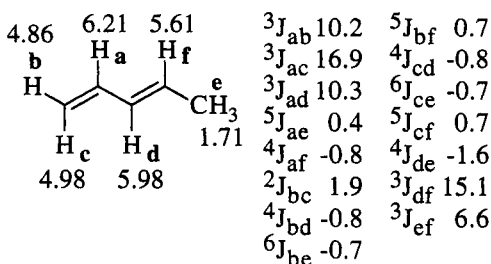
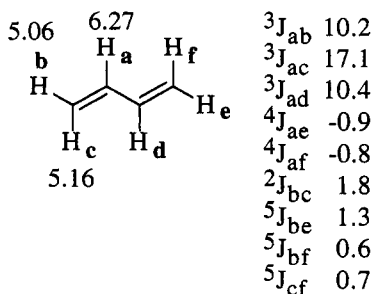
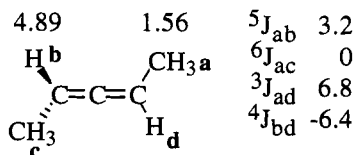
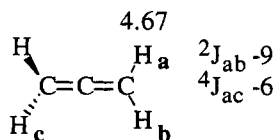
1) The increment for "alkyl ring" is to be used if the substituent and the double bond are part of a cyclic structure.

2) The increment "conjugated" is to be used if either the double bond or the substituent is conjugated to other substituents.

3) The increment "aromatic, fixed" is to be used if the double bond conjugated to an aromatic ring is part of a fused ring (such as in 1,2-dihydronaphthalene).

¹H Chemical Shifts of Substituted Isobutenes (δ in ppm relative to TMS)



^1H Chemical Shifts of Enols (δ in ppm relative to TMS, J in Hz)**5.2.2
Dienes** **^1H Chemical Shifts and Coupling Constants of Conjugated Dienes (δ in ppm relative to TMS, J in Hz)** **^1H Chemical Shifts and Coupling Constants of Allenes (δ in ppm relative to TMS, J in Hz)**

5.4 Alicyclics

^1H Chemical Shifts and Coupling Constants of Saturated Alicyclic Hydrocarbons (δ in ppm relative to TMS, J in Hz)



0.20

 $2J_{\text{gem}} -4.3$ $3J_{\text{cis}} 9.0$ $3J_{\text{trans}} 5.6$

In derivatives:

 $2J_{\text{gem}} -3$ to -9 $3J_{\text{cis}} 6$ to 12 $3J_{\text{trans}} 2$ to 9

Throughout:

 $J_{\text{cis}} > J_{\text{trans}}$ 

1.94

In derivatives:

 $2J_{\text{gem}} -10$ to -17 $3J_{\text{cis}} 4$ to 12 $3J_{\text{trans}} 2$ to 10 $4J_{\text{cis}} \approx 0$ $4J_{\text{trans}} \approx -1$ 

1.51

In derivatives:

 $2J_{\text{gem}} -8$ to -18 $3J_{\text{cis}} 5$ to 10 $3J_{\text{trans}} 5$ to 10 

1.44

In derivatives:

 $2J_{\text{gem}} -11$ to -14 $3J_{\text{ax,ax}} 8$ to 13 $3J_{\text{eq,ax}} 2$ to 6 $3J_{\text{eq,eq}} 2$ to 5

Generally:

 $J_{\text{eq,ax}} \approx J_{\text{eq,eq}} + 1$ At -100°C : $H_{\text{ax}} 1.1$ $H_{\text{eq}} 1.6$ 

b

7.01

a

0.92

In derivatives:

 $3J_{\text{ab}} 1.5$ to 2.0 $3J_{\text{bc}} 0.5$ to 1.5 

b

5.95

d

2.57

 $2J_{\text{gem}} -13.7$ $3J_{\text{ab}} 1.0$ $4J_{\text{ac}} -0.3$ $3J_{\text{ad,cis}} 1.8$ $3J_{\text{ad,trans}} 4.6$ $3J_{\text{bc}} 2.8$ 

c

5.66

e

2.27

a

1.79

 $2J_{\text{gem,a}} -12.8$ $3J_{\text{ab,cis}} 9.3$ $3J_{\text{ab,trans}} 5.7$ $2J_{\text{gem,b}} -16.1$ $3J_{\text{bc}} 2.3$ $4J_{\text{bd}} -2.3$ $5J_{\text{be,cis}} 2.1$ $5J_{\text{be,trans}} 3.0$ $3J_{\text{cd}} 5.8$ 

c

6.43

e

6.28

a

2.80

 $3J_{\text{ab}} 1.3$ $4J_{\text{ac}} -1.5$ $3J_{\text{bc}} 5.0$ $4J_{\text{bd}} 1.1$ $5J_{\text{be}} 2.0$ $3J_{\text{cd}} 1.9$ 

a

6.53

e

6.22

b

5.85

H_dH_c $3J_{\text{ab}} 5.1$ $5J_{\text{ac}} 0.5$ $5J_{\text{ad}} 1.4$ $4J_{\text{ae}} 1.3$ $3J_{\text{af}} 2.0$ $4J_{\text{bc}} -0.2$ $4J_{\text{bd}} -0.4$ $4J_{\text{be}} 2.0$ $2J_{\text{cd}} 0.1$ 

a

5.59

b

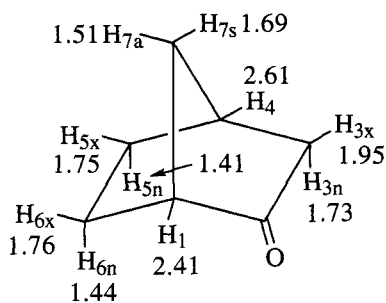
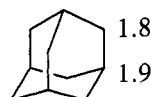
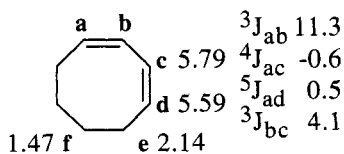
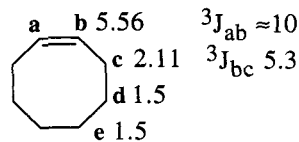
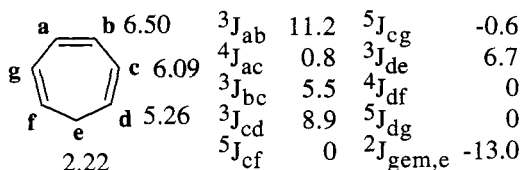
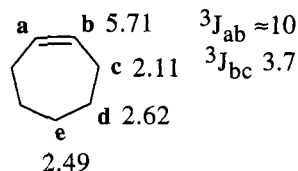
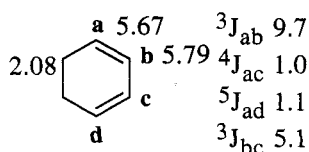
1.96

c

1.65

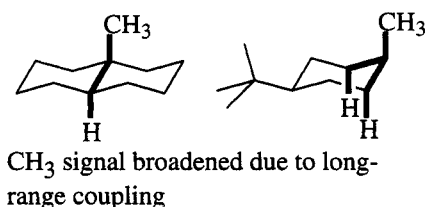
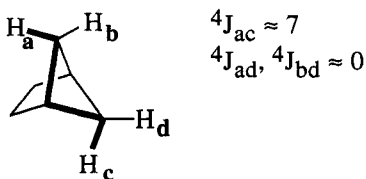
d

 $3J_{\text{ab}} \approx 10$ $3J_{\text{bc}} 1.5$

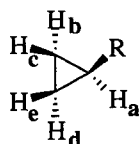


$^4J_{1,4}$	1.2	$^4J_{4,6n}$	-0.5
$^4J_{1,5n}$	-0.3	$^4J_{4,6x}$	0.7
$^4J_{1,5x}$	0.2	$^3J_{4,7a}$	2.1
$^3J_{1,6n}$	0.1	$^3J_{4,7s}$	1.6
$^3J_{1,6x}$	4.7	$^2J_{5n,5x}$	-12.8
$^3J_{1,7a}$	1.2	$^3J_{5n,6n}$	9.1
$^3J_{1,7s}$	1.6	$^3J_{5n,6x}$	4.7
$^2J_{3n,3x}$	-17.6	$^4J_{5n,7a}$	-0.1
$^3J_{3n,4}$	0	$^4J_{5n,7s}$	2.1
$^4J_{3n,7a}$	4.2	$^3J_{5x,6n}$	4.6
$^4J_{3n,7a}$	4.2	$^3J_{5x,6x}$	12.1
$^3J_{3x,4}$	4.8	$^2J_{6n,6x}$	-12.3
$^4J_{3x,5x}$	2.3	$^4J_{6n,7a}$	-0.1
$^3J_{4,5n}$	0.1	$^4J_{6n,7s}$	2.3
$^3J_{4,5x}$	4.3	$^2J_{7a,7s}$	-10.2

In condensed alicyclics, couplings over four or more bonds are often observed. Such long-range couplings are particularly large if the arrangement of the bonds between the two protons is w-shaped:

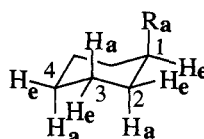
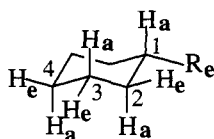


^1H Chemical Shifts and Coupling Constants of Monosubstituted Cyclopropanes (δ in ppm relative to TMS, J in Hz)



Substituent X	H _a	H _{b,d}	H _{c,e}	$^3J_{ab}$	$^3J_{ac}$	$^2J_{bc}$	$^3J_{bd}$	$^3J_{be}$	$^3J_{ce}$
-H	0.20	0.20	0.20	9.0	5.6	-4.3	9.0	5.6	9.0
C -CH=CH ₂	2.36	0.64	0.34	8.2	4.9	-4.5	9.3	6.2	9.0
-phenyl	1.71	2.65	2.83	9.5	6.3	-4.5	9.5	5.2	8.9
H -F	4.32	0.69	0.27	5.9	2.4	-6.7	10.8	7.7	12.0
a -Cl	2.55	0.87	0.74	7.0	3.6	-6.0	10.3	7.1	10.6
l -Br	2.83	0.96	0.81	7.1	3.8	-6.1	10.2	7.0	10.5
-I	2.31	1.04	0.76	7.5	4.4	-5.9	9.9	6.6	10.0
O -OH	3.35	0.59	0.34	6.2	2.9	-5.4	10.3	6.8	10.9
N -NH ₂	2.23	0.32	0.20	6.6	3.6	-4.3	9.7	6.2	9.9
-CN	1.36	0.94	0.93	8.4	5.1	-4.7	9.2	7.1	9.5
O -CO-cyclopropyl	1.70	0.56	1.02	7.9	4.6	-3.5	9.1	7.0	9.5
-COOH	1.59	0.91	1.05	8.0	4.6	-4.0	9.3	7.1	9.7
C -COOCH ₃	1.95	0.81	0.85	8.0	4.6	-3.4	8.8	6.9	9.6
/ \ -COF	1.66	1.20	1.11	8.0	4.6	-4.5	10.1	7.5	9.3
-COCl	2.11	1.18	1.28	7.9	4.4	-4.5	9.2	7.6	10.0
-Li	-2.53	0.43	-0.12	10.3	9.1	-1.6	7.7	3.2	6.5
-B(cyclopropyl) ₂	-0.25	0.66	0.61	8.9	5.8	-3.3	8.2	5.9	8.4
-Hg-cyclopropyl	0.00	0.75	0.47	9.6	6.9	-3.7	8.5	4.8	7.9

¹H Chemical Shifts of Axially and Equatorially Monosubstituted Cyclohexanes (δ in ppm relative to TMS)



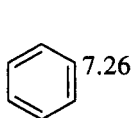
Substituent R	1a	2a	2e	3a	3e	1e	2a	2e	3a	3e
-D	1.12	1.12	1.60	1.12	1.60	1.60	1.12	1.60	1.12	1.60
C -CH ₃	1.27	0.81	1.57	1.15	1.60	1.93	1.37	1.40	1.39	1.34
-phenyl	2.47					2.98				
H -Cl	3.63					4.34			1.7	
a -Br	3.81					4.62				
l -I	3.98					4.72				
O -OH	3.38	1.09	1.78	1.19	1.61	3.89	1.35	1.58	1.58	1.33
-OCOCH ₃	4.46					4.98	1.47	2.3		
N -NH ₂	2.52					3.15				
-NHCH ₃	2.08					2.70				
-NO ₂	4.23	2.2	1.9			4.43	1.6	2.6		
S -SH	2.57	0.7	1.3			3.43		1.5	1.9	



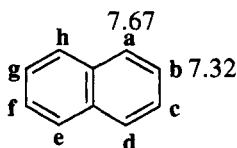
5.5

Aromatic Hydrocarbons

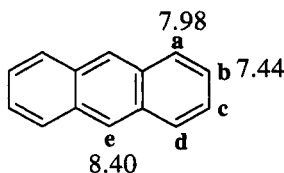
^1H Chemical Shifts and Coupling Constants of Aromatic Hydrocarbons (δ in ppm relative to TMS, J in Hz)



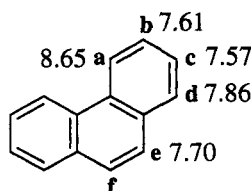
In derivatives:
 $^3J_{\text{ortho}}$ 6.5–8.5
 $^4J_{\text{meta}}$ 1.0–3.0
 $^5J_{\text{para}}$ 0.0–1.0



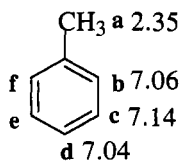
In derivatives:
 $^3J_{\text{ab}}$ 8–9
 $^4J_{\text{ac}}$ 1–2
 $^5J_{\text{ad}}$ \approx 1
 $^3J_{\text{bc}}$ 5–7
 $^5J_{\text{ae}}$ \approx 0.9
 $^6J_{\text{af}}$ \approx 0.1
 $^5J_{\text{ag}}$ \approx 0.2
 $^4J_{\text{ah}}$ \approx 0.5
 $^7J_{\text{bf}}$ \approx 0.3
 $^6J_{\text{bg}}$ \approx 0.1



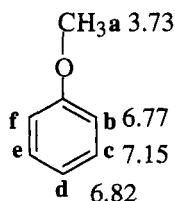
In derivatives:
 $^3J_{\text{ab}}$ 8.5–9.5
 $^4J_{\text{ac}}$ 0.8–1.5
 $^5J_{\text{ad}}$ 0.6–0.9
 $^5J_{\text{ae}}$ \approx 0.8
 $^3J_{\text{bc}}$ 6.5–8.0
 $^4J_{\text{de}}$ \approx 0.4



$^3J_{\text{ab}}$ 8.4
 $^4J_{\text{ac}}$ 1.2
 $^5J_{\text{ad}}$ 0.7
 $^3J_{\text{bc}}$ 7.2
 $^4J_{\text{bd}}$ 1.3
 $^3J_{\text{cd}}$ 8.1
 In derivatives:
 $^3J_{\text{ef}}$ \approx 9

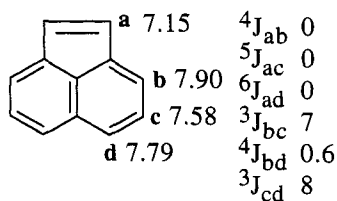
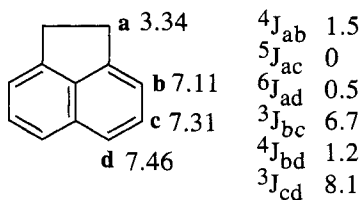
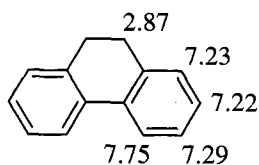
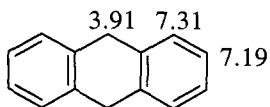
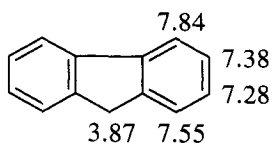
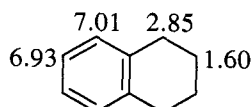
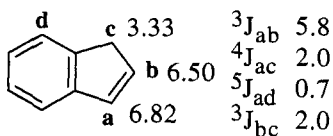
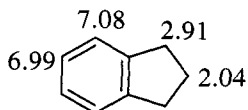
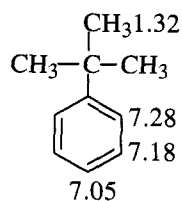
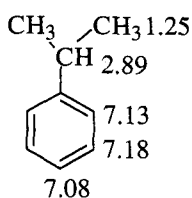
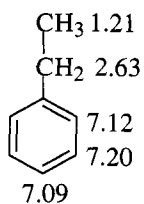


$^4J_{\text{ab}}$ -0.7
 $^5J_{\text{ac}}$ 0.3
 $^6J_{\text{ad}}$ -0.6
 $^3J_{\text{bc}}$ 7.7
 $^4J_{\text{bd}}$ 1.3
 $^5J_{\text{be}}$ 0.6
 $^4J_{\text{bf}}$ 2.0
 $^3J_{\text{cd}}$ 7.5
 $^4J_{\text{ce}}$ 1.5

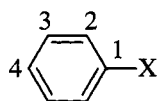


$^5J_{\text{ab}}$ \approx 0.8
 $^3J_{\text{bc}}$ 8.3
 $^4J_{\text{bd}}$ 1.0
 $^5J_{\text{be}}$ 0.4
 $^4J_{\text{bf}}$ 2.7
 $^3J_{\text{cd}}$ 7.4
 $^4J_{\text{ce}}$ 1.8

In routine spectra, the small long-range couplings between aromatic protons and aliphatic substituents are not resolved. Nevertheless, they are diagnostically highly relevant because the line broadenings caused by them are easily detected (if there is a reference line in the spectrum, e.g. from another methyl group, or in an AA'XX' spin system of the aromatic protons). As a confirmation, a decoupling experiment may be useful (line sharpening on weak irradiation of the frequency of the coupling partner) or a COSY experiment is recommended.



Effect of Substituents on ^1H Chemical Shifts of Monosubstituted Benzenes (in ppm relative to TMS)



$$\delta_{\text{H}_i} = 7.26 + Z_i$$

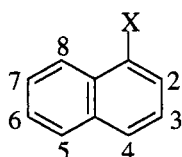
Substituent X	Z_2	Z_3	Z_4
-H	0.00	0.00	0.00
C -CH ₃	-0.20	-0.12	-0.21
-CH ₂ CH ₃	-0.14	-0.05	-0.18
-CH(CH ₃) ₂	-0.13	-0.08	-0.18
-C(CH ₃) ₃	0.03	-0.08	-0.20
-CF ₃	0.19	-0.07	0.00
-CCl ₃	0.55	-0.07	-0.09
-CH ₂ OH	-0.07	-0.07	-0.07
-CH=CH ₂	0.04	-0.05	-0.12
-CH=CH-phenyl (<i>trans</i>)	0.16	0.00	-0.15
-C≡CH	0.16	-0.03	-0.02
-C≡C-phenyl	0.20	-0.04	-0.07
-phenyl	0.22	0.06	-0.04
-2-pyridyl	0.73	0.09	0.02
H -F	-0.29	-0.02	-0.23
a -Cl	0.01	-0.06	-0.12
I -Br	0.17	-0.11	-0.06
-I	0.38	-0.23	-0.01
O -OH	-0.53	-0.17	-0.44
-OCH ₃	-0.49	-0.11	-0.44
-OCH ₂ CH=CH ₂	-0.45	-0.13	-0.43
-O-phenyl	-0.34	-0.04	-0.28
-OCOCH ₃	-0.19	-0.03	-0.19
-OCO-phenyl	-0.11	0.07	-0.10
-OSO ₂ CH ₃	-0.05	0.07	-0.01
N -NH ₂	-0.80	-0.25	-0.64
-NHCH ₃	-0.83	-0.22	-0.68
-N(CH ₃) ₂	-0.67	-0.18	-0.66
-N ⁺ (CH ₃) ₃ I ⁻	0.72	0.40	0.34
-NHCOCH ₃	0.38	-0.02	-0.26
-NHNH ₂	-0.60	-0.08	-0.55
-N=N-phenyl	0.67	0.20	0.20
-NO	0.55	0.29	0.35
-NO ₂	0.93	0.26	0.39
-CN	0.25	0.18	0.30
-NCS	-0.11	0.04	-0.02



Substituent X	Z ₂	Z ₃	Z ₄
S -SH	-0.08	-0.16	-0.22
-SCH ₃	-0.08	-0.10	-0.24
-S-phenyl	-0.06	-0.20	-0.26
-S-S-phenyl	0.24	0.02	-0.06
-SO ₂ CH ₃	0.68	0.35	0.39
-SO ₂ OCH ₃	0.68	0.34	0.36
-SO ₂ Cl	0.68	0.23	0.34
-SO ₂ NH ₂	0.59	0.32	0.32
O -CHO	0.61	0.25	0.35
 -COCH ₃	0.60	0.11	0.19
C -COCH ₂ CH ₃	0.63	0.08	0.18
/\ -CO-phenyl	0.44	0.10	0.19
-CO-(2-pyridyl)	0.86	0.11	0.20
-COOH	0.87	0.21	0.34
-COOCH(CH ₃) ₂	0.73	0.11	0.20
-COO-phenyl	0.88	0.15	0.25
-CONH ₂	0.69	0.18	0.25
-COF	0.71	0.21	0.38
-COCl	0.81	0.21	0.37
-COBr	0.77	0.21	0.38
-CH=N-phenyl	0.64	0.24	0.24
-Li	0.77	0.26	-0.29
-MgBr	0.40	-0.19	-0.26
-Mg-phenyl	-0.49	0.18	0.25
-Si(CH ₃) ₃	0.19	0.00	0.00
-Si(phenyl) ₂ Cl	0.32	0.07	0.12
-SiCl ₃	0.52	≈0.2	≈0.2
P -Pb(phenyl) ₂ Cl	0.68	0.28	0.11
-P(phenyl) ₂	-0.02	-0.33	-0.33
-PO(OCH ₃) ₂	0.46	0.14	0.22
-Zn-phenyl	-0.36	0.02	0.05
-Hg-phenyl	0.00	0.00	-0.20



Effect of Substituents in Position 1 on the ^1H Chemical Shifts of Monosubstituted Naphthalenes (in ppm relative to TMS)



for X : H $\delta_{\text{H}_1}, \delta_{\text{H}_4}, \delta_{\text{H}_5}, \delta_{\text{H}_8}$: 7.67

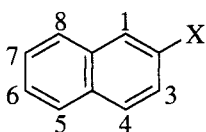
$\delta_{\text{H}_2}, \delta_{\text{H}_3}, \delta_{\text{H}_6}, \delta_{\text{H}_7}$: 7.32



Substituent X	H-2	H-3	H-4	H-5	H-6	H-7	H-8
C -CH ₃	-0.22	-0.13	-0.16	-0.03	-0.03	-0.01	0.10
-CH ₂ CH ₃	0.01	0.08	0.03	0.17	0.14	0.17	0.38
-CH ₂ C≡CH	0.25	-0.07	-0.06	0.00	0.03	0.13	0.69
-CH ₂ Cl	0.13	0.01	0.09	0.13	0.14	0.20	0.42
-CF ₃	0.67	0.15	0.18	0.23	0.23	0.29	0.52
H -F	-0.22	0.01	-0.11	0.13	0.15*	0.17*	0.42
a -Cl	0.17	-0.04	-0.02	0.07	0.11	0.16	0.54
l -Br	0.38	-0.09	0.03	0.05	0.11	0.19	0.51
-I	0.10	-0.48	0.18	-0.20	-0.07	-0.02	0.27
O -OH	-0.68	-0.15	-0.36	0.01	0.03	0.06	0.41
-OCH ₃	-0.68	-0.09	-0.38	-0.01	0.04	0.03	0.50
-OCOCH ₃	-0.15	0.11	-0.10	0.03	-0.07	0.07	0.16
N -NH ₂	-0.77	-0.17	-0.51	-0.06	-0.02	-0.01	-0.01
-N(CH ₃) ₂	-0.30	0.03	-0.19	0.11	0.13	0.10	0.55
-NHCOCH ₃	0.40	0.17	0.05	0.26	0.20	0.24	0.44
-NO ₂	0.80	0.14	0.19	0.33	0.21	0.32	0.72
-NCO	-0.29	-0.15	-0.19	-0.03	0.05	0.03	0.24
-CN	0.48	0.12	0.30	0.16	0.22	0.29	0.51
O -CHO	0.44	0.10	0.21	0.06	0.14	0.23	1.52
 -COCH ₃	0.38	-0.07	0.10	0.01	0.04	0.13	1.08
C -COOH	1.11	0.23	0.42	0.24	0.25	0.34	1.43
/\ -COOCH ₃	0.80	0.05	0.22	0.08	0.10	0.20	1.30
-COCl	1.17	0.17	0.37	0.17	0.21	0.30	1.04

* Assignment uncertain

Effect of Substituents in Position 2 on the ^1H Chemical Shifts of Monosubstituted Naphthalenes (in ppm relative to TMS)



for X: H $\delta_{\text{H}1}, \delta_{\text{H}4}, \delta_{\text{H}5}, \delta_{\text{H}8}$: 7.67

$\delta_{\text{H}2}, \delta_{\text{H}3}, \delta_{\text{H}6}, \delta_{\text{H}7}$: 7.32


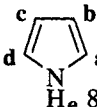

Substituent X	H-1	H-3	H-4	H-5	H-6	H-7	H-8
C $-\text{CH}_3$	-0.21	-0.14	-0.06	0.01	-0.04	-0.01	-0.03
$-\text{CH}_2\text{CH}_3$	-0.05	0.02	0.09	0.12	0.08	0.12	0.10
$-\text{CH}(\text{CH}_3)_2$	-0.07	0.01	0.05	0.07	0.04	0.06	0.07
$-\text{CH}=\text{CH}_2$	0.06	0.30	0.11	0.11	0.10	0.12	0.11
$-\text{CF}_3$	0.45	0.30	0.23		0.25	0.22	
$-\text{Cl}$	0.13	0.08	0.07	0.12	0.13	0.15	0.05
$-\text{Br}$	0.23	0.14	-0.09	-0.08	0.05	0.07	0.01
O $-\text{OH}$	-0.69	-0.35	-0.05	-0.04	-0.11	-0.02	-0.14
$-\text{OCH}_3$	-0.70	-0.28	-0.07	-0.03	-0.11	0.00	-0.07
$-\text{OCOCH}_3$	-0.19	-0.14	0.01	0.06	-0.04	0.11	0.08
N $-\text{NH}_2$	-0.88	-0.56	-0.16	-0.12	-0.23	-0.09	-0.23
$-\text{N}(\text{CH}_3)_2$	-0.90	-0.33	-0.13	-0.12	-0.23	-0.08	-0.16
$-\text{NHCOCCH}_3$	0.50	0.14	0.07	0.06	0.07	0.10	0.08
$-\text{NO}_2$	0.98	0.82	0.18	0.18	0.28	0.24	0.26
$-\text{CN}$	0.51	0.25	0.20	0.19	0.31	0.26	0.19
O $-\text{CHO}$	0.62	0.61	0.23	0.21	0.30	0.24	0.29
 $-\text{COCH}_3$	0.76	0.69	0.19	0.17	0.25	0.21	0.26
C $-\text{COOH}$	1.00	0.73	0.37	0.36	0.36	0.32	0.48
/\ $-\text{COOCH}_3$	0.83	0.66	0.09	0.09	0.15	0.11	0.17
$-\text{COCl}$	1.02	0.74	0.39	0.49	0.32	0.37	0.37





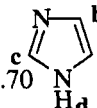
5.6 Heteroaromatic Compounds

5.6.1 Non-Condensed Heteroaromatic Rings



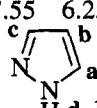
^1H Chemical Shifts and Coupling Constants of Non-Condensed Heteroaromatic Compounds (δ in ppm relative to TMS, $|J|$ in Hz)

	δ b 6.30 a 7.38	$^3J_{ab}$ 1.8 $^4J_{ac}$ 0.9 $^4J_{ad}$ 1.5 $^3J_{bc}$ 3.4		δ b 6.05 a 6.62 NH e 8 (broad)	$^3J_{ab}$ 2.6 $^4J_{ac}$ 1.3 $^4J_{ad}$ 2.1 $^3J_{ae}$ 2.6 $^3J_{bc}$ 3.5 $^4J_{be}$ 2.3		δ b 6.96 a 7.20	$^3J_{ab}$ 4.8 $^4J_{ac}$ 1.0 $^4J_{ad}$ 2.8 $^3J_{bc}$ 3.5
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


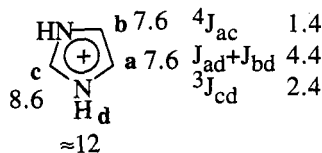
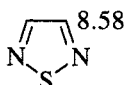
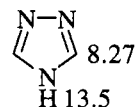
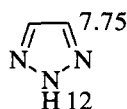
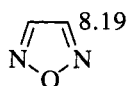
	δ b 7.12 a 7.70	$^3J_{ab}$ 5.4 $^4J_{ac}$ 1.1 $^4J_{ad}$ 2.5 $^3J_{bc}$ 3.6		δ b 7.09 a 7.69 c 7.95	$^3J_{ab}$ 0.8 $^4J_{ac}$ 0.5 $^4J_{bc}$ 0.0		δ b 7.13 a 7.13 H d 13.4	$^3J_{ab}$ 1-2 $^4J_{ac}$ 1-2 $^3J_{bc} \approx 1$
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(J values in derivatives)

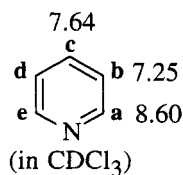
	δ b 7.98 a 7.41 c 8.88	$^3J_{ab}$ 3.2 $^4J_{ac}$ 1.9 $^3J_{bc}$ 0.0		δ b 6.28 a 8.39 c 8.15	$^3J_{ab}$ 1.7 $^4J_{ac}$ 0.3 $^4J_{bc}$ 1.8		δ b 6.25 a 7.55 H d 13.7 c 7.55	$^3J_{ab}$ 2.1 $^4J_{ac}$ 0.0 $^3J_{bc}$ 2.1
--	-------------------------------------	--	--	-------------------------------------	--	--	---	--

(in CS_2)

	δ b 7.26 a 8.72 c 8.56	$^3J_{ab}$ 4.7 $^4J_{ac} < 0.4$ $^3J_{bc}$ 1.7
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(in H_2SO_4)

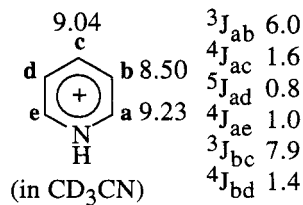


In DMSO:

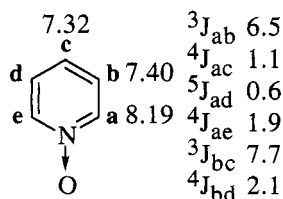
a 8.59
 b 7.38
 c 7.75

In derivatives:

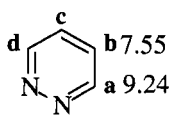
$^3J_{ab}$ 6.0 4–6
 $^4J_{ac}$ 1.9 0–2.5
 $^5J_{ad}$ 0.9 0–2.5
 $^4J_{ae}$ 0.4 0–0.6
 $^3J_{bc}$ 7.6 7–9
 $^4J_{bd}$ 1.6 0.5–2



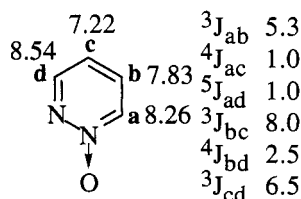
$^3J_{ab}$ 6.0
 $^4J_{ac}$ 1.6
 $^5J_{ad}$ 0.8
 $^4J_{ae}$ 1.0
 $^3J_{bc}$ 7.9
 $^4J_{bd}$ 1.4



$^3J_{ab}$ 6.5
 $^4J_{ac}$ 1.1
 $^5J_{ad}$ 0.6
 $^4J_{ae}$ 1.9
 $^3J_{bc}$ 7.7
 $^4J_{bd}$ 2.1

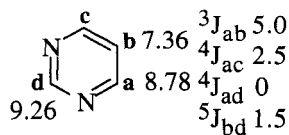


$^3J_{ab}$ 4.9
 $^4J_{ac}$ 2.0
 $^5J_{ad}$ 3.5
 $^3J_{bc}$ 8.4

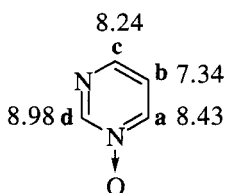


$^3J_{ab}$ 5.3
 $^4J_{ac}$ 1.0
 $^5J_{ad}$ 1.0
 $^3J_{bc}$ 8.0
 $^4J_{bd}$ 2.5
 $^3J_{cd}$ 6.5

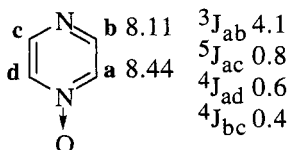
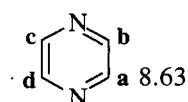
(in acetone)



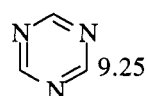
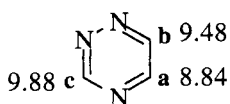
$^3J_{ab}$ 5.0
 $^4J_{ac}$ 2.5
 $^4J_{ad}$ 0
 $^5J_{bd}$ 1.5



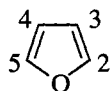
$^3J_{ab}$ 6.8
 $^4J_{ac}$ 1.6
 $^4J_{ad}$ 2.0
 $^3J_{bc}$ 4.9
 $^5J_{bd}$ 1.0
 $^4J_{cd}$ 0



$^3J_{ab}$ 4.1
 $^5J_{ac}$ 0.8
 $^4J_{ad}$ 0.6
 $^4J_{bc}$ 0.4



Effect of Substituents on the ^1H Chemical Shifts of Mono-substituted Furans (in ppm relative to TMS)



$$\delta_{\text{H-2}} = 7.38 + Z_{i,2}$$

$$\delta_{\text{H-3}} = 6.30 + Z_{i,3}$$

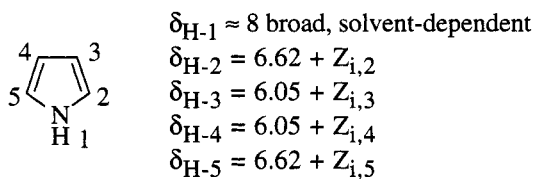
$$\delta_{\text{H-4}} = 6.30 + Z_{i,4}$$

$$\delta_{\text{H-5}} = 7.38 + Z_{i,5}$$

Substituent	in position 2 or 5:			in position 3 or 4:		
	Z_{23} Z_{54}	Z_{24} Z_{53}	Z_{25} Z_{52}	Z_{32} Z_{45}	Z_{34} Z_{43}	Z_{35} Z_{42}
-H	0.00	0.00	0.00	0.00	0.00	0.00
C -CH ₃	-0.42	-0.12	-0.17	-0.27	-0.17	-0.15
-CH ₂ OH	-0.11	-0.05	-0.08			
-CH ₂ NH ₂	-0.24	-0.06	-0.10			
-CH=CHCHO	0.70	0.35	0.42			
-Br	-0.02	0.03	-0.01			
-I	0.12	-0.13	-0.01	-0.13	0.04	-0.22
O -OCH ₃	-1.34	-0.23	-0.68	-0.46	-0.28	-0.37
N -NO ₂	1.21	0.55	0.51			
-CN	0.85	0.32	0.28	0.45	0.22	-0.02
S -SCH ₃	-0.12	-0.06	-0.09	-0.18	-0.05	-0.15
-SCN	0.40	0.06	0.10	0.19	0.19	0.03
O -CHO	0.93	0.31	0.34	0.48	0.37	-0.07
 -COCH ₃	0.81	0.23	0.19	0.46	0.36	-0.12
C -COCF ₃	1.34	0.50	0.64			
/\ -COOH	0.94	0.33	0.41	0.89	0.54	0.36
-COOCH ₃	0.85	0.22	0.25	0.45	0.33	-0.14
-COCl	1.20	0.39	0.48			



Effect of Substituents on the ^1H Chemical Shifts of Mono-substituted Pyrroles (in ppm relative to TMS)

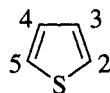


Substituent in position 1	Z_{12} Z_{15}	Z_{13} Z_{14}
-H	0.00	0.00
-CH ₃	-0.25	-0.13
-CH ₂ CH ₃	-0.16	-0.12
-CH ₂ -phenyl	-0.12	-0.04
-phenyl	0.33	0.14
-COCH ₃	0.56	0.12
-CO-phenyl	0.57	0.18



Substituent	in position 2 or 5:			in position 3 or 4:		
	Z_{23} Z_{54}	Z_{24} Z_{53}	Z_{25} Z_{52}	Z_{32} Z_{45}	Z_{34} Z_{43}	Z_{35} Z_{42}
-H	0.00	0.00	0.00	0.00	0.00	0.00
C -CH ₃	-0.33	-0.16	-0.26	-0.34	-0.20	-0.20
N -NO ₂	1.06	0.24	0.43	1.04	0.70	0.13
-CN	0.83	0.23	0.51			
S -SCH ₃	0.18	0.05	0.10			
-SCN	0.48	0.10	0.28			
O -CHO	0.93	0.27	0.61			
 -COCH ₃	0.78	0.10	0.44	0.79	0.63	0.15
C -COOCH ₃	0.79	0.13	0.29	0.90	0.73	0.16

Effect of Substituents on the ^1H Chemical Shifts of Mono-substituted Thiophenes (in ppm relative to TMS)



$$\delta_{\text{H-2}} = 7.20 + Z_{i,2}$$

$$\delta_{\text{H-3}} = 6.96 + Z_{i,3}$$

$$\delta_{\text{H-4}} = 6.96 + Z_{i,4}$$

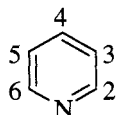
$$\delta_{\text{H-5}} = 7.20 + Z_{i,5}$$

Substituent	in position 2 or 5:			in position 3 or 4:		
	Z_{23} Z_{54}	Z_{24} Z_{53}	Z_{25} Z_{52}	Z_{32} Z_{45}	Z_{34} Z_{43}	Z_{35} Z_{42}
-H	0.00	0.00	0.00	0.00	0.00	0.00
C -CH ₃	-0.36	-0.24	-0.29	-0.45	-0.22	-0.14
-C≡CH	0.15	-0.16	-0.12			
H -Cl	-0.25	-0.22	-0.22	-0.22	-0.11	-0.03
a -Br	-0.05	-0.27	-0.11	-0.12	-0.08	-0.10
I -I	0.13	-0.33	0.01	0.06	0.00	-0.19
O -OH*	-0.72	0.59	-3.10			
-OCH ₃	-0.94	-0.43	-0.82	-1.10	-0.38	-0.20
N -NH ₂	-0.95	-0.45	-0.85	-1.25	-0.53	-0.25
-NO ₂	0.82	-0.03	0.30	0.95	0.60	0.03
-CN	0.47	0.00	0.28	0.63	0.20	0.15
S -SH	0.00	-0.20	-0.07	-0.22	-0.20	-0.10
-SCH ₃	-0.03	-0.18	-0.05	-0.33	-0.10	-0.03
-SO ₂ CH ₃	1.03	0.20	0.79	0.96	0.48	0.46
-SO ₂ Cl	0.73	0.06	0.45			
-SCN	0.30	-0.05	0.28	0.25	0.05	0.05
O -CHO	0.65	0.10	0.45	0.79	0.45	0.03
 -COCH ₃	0.57	0.00	0.28	0.68	0.47	-0.02
C -COOH	0.80	0.08	0.40	0.99	0.48	0.24
/\ -COOCH ₃	0.70	-0.05	0.20	0.78	0.47	-0.05
-COCl	0.88	0.06	0.44	1.05	0.50	0.03

* Present in the keto form



Effect of Substituents on the ^1H Chemical Shifts of Mono-substituted Pyridines (in ppm relative to TMS; solvent: DMSO)



$$\delta_{\text{H-2}} = 8.59 + Z_{i,2}$$

$$\delta_{\text{H-3}} = 7.38 + Z_{i,3}$$

$$\delta_{\text{H-4}} = 7.75 + Z_{i,4}$$

$$\delta_{\text{H-5}} = 7.38 + Z_{i,5}$$

$$\delta_{\text{H-6}} = 8.59 + Z_{i,6}$$

Substituent in position 2 or 6		Z_{23} Z_{65}	Z_{24} Z_{64}	Z_{25} Z_{63}	Z_{26} Z_{62}
C	-H	0.00	0.00	0.00	0.00
	-CH ₃	-0.11	-0.01	-0.16	0.08
	-CH ₂ CH ₃	-0.09	-0.08	-0.15	0.03
	-CH ₂ -phenyl	0.12	-0.08	-0.20	0.02
	-CH ₂ OH	0.37	0.30	0.02	0.06
	-CH ₂ NH ₂	0.20	0.07	-0.09	0.05
	-CH ₂ S- <i>n</i> -C ₃ H ₇	0.04	-0.08	-0.26	-0.06
	-CH ₂ SO ₂ -phenyl	≈0	≈-0.3	≈0	-0.2
	-CH=CH ₂	0.11	-0.14	-0.11	0.04
	-phenyl	0.16	-0.28	-0.40	-0.03
H a l	-2-pyridyl	1.12	-0.09	-0.26	0.00
	-F	-0.10	0.40	0.12	-0.13
	-Cl	0.32	0.29	0.29	0.20
	-Br	0.41	0.17	0.19	0.02
O	-OH	-0.7	0.0	-1.0	-0.9
	-O- <i>n</i> -C ₄ H ₉	-0.53	-0.03	-0.49	-0.32
N	-NH ₂	-0.68	-0.31	-0.78	-0.48
	-NHCOCH ₃	0.94	0.16	-0.20	-0.10
	-NHCOOCH ₂ CH ₃	0.59	0.07	-0.24	-0.21
	-NHNO ₂	0.34	0.31	-0.03	-0.41
	-NO ₂	1.09	0.67	0.74	0.26
	-CN	0.88	0.38	0.55	0.39
S	-SCH ₃	-0.09	-0.11	-0.29	-0.11
O	-CHO	0.93	0.42	0.50	0.44
	-COCH ₃	0.82	0.37	0.39	0.28
C	-CO-phenyl	0.62	0.55	0.32	0.28
/\	-COOH	0.97	0.43	0.48	0.42
	-COO- <i>n</i> -C ₄ H ₉	0.86	0.39	0.35	0.35
	-CONH ₂	1.05	0.47	0.43	0.30
	-CSNH ₂	1.41	0.37	0.33	0.25
	-CH=NÖH	0.40	0.28	0.01	0.16



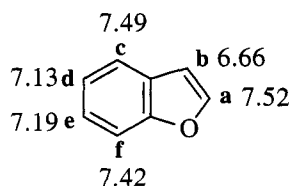
Substituent	in position 3 or 5:				in position 4:	
	Z_{32} Z_{56}	Z_{34} Z_{54}	Z_{35} Z_{53}	Z_{36} Z_{52}	Z_{42} Z_{46}	Z_{43} Z_{45}
-H	0.00	0.00	0.00	0.00	0.00	0.00
C -CH ₃	-0.02	-0.06	-0.09	-0.02	0.01	-0.10
-CH ₂ -phenyl					0.00	-0.15
-CH ₂ OH	0.11	0.15	0.04	-0.04	0.07	0.14
-CH ₂ NH ₂	0.16	0.13	0.04	0.00	0.01	0.03
-CH ₂ S- <i>n</i> -C ₃ H ₇					-0.06	-0.13
-CH ₂ SO ₂ -phenyl	-0.24	-0.15	-0.22	0.01	-0.09	-0.18
-CH=CH ₂					0.12	0.13
-CH=CH-COOH	0.45	0.52	0.34	0.17		
H -F	-0.01	0.00	0.14	-0.10	-0.07	-0.03
a -Cl	0.20	0.24	0.19	0.09	0.00	0.05
I -Br	0.20	0.43	0.34	0.18	0.09	0.35
O -OH	-0.03	-0.37	0.15	-0.24		
-OCH ₃					0.02	-0.29
N -NH ₂	-0.06	-0.49	0.02	-0.36	-0.15	-0.74
-NHCOCH ₃	0.37	0.50	0.06	-0.16	-0.05	0.31
-CN	0.63	0.72	0.43	0.50	0.46	0.62
S -SCH ₂ -phenyl					-0.02	0.04
-S-phenyl					0.05	-0.16
-SO ₃ H	0.70	1.14	0.81	0.70		
O -CHO	0.45	0.42	0.12	0.20	0.47	0.58
 -COCH ₃	0.72	0.68	0.30	0.37	0.40	0.58
C -CO-phenyl	0.47	0.54	0.37	0.34	0.36	0.40
/\ -COOCH ₃	0.62	0.60	0.23	0.34		
-COO- <i>n</i> -C ₄ H ₉					0.34	0.54
-CSNH ₂	0.68	0.67	0.24	0.26	0.35	0.68
-CH=NOH	0.39	0.43	0.19	0.15	0.24	0.37



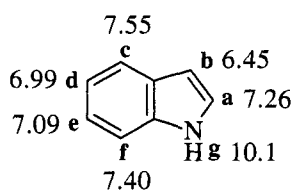
5.6.2

Condensed Heteroaromatic Rings

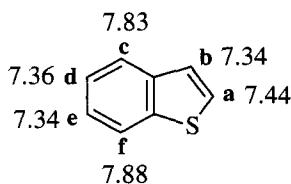
¹H Chemical Shifts of Condensed Heteroaromatic Rings
(δ in ppm relative to TMS, $|J|$ in Hz)



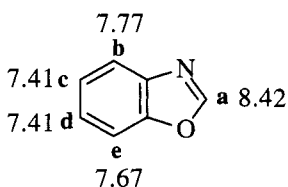
$^3J_{ab}$ 2.5	$^4J_{ce}$ 1.2
$^5J_{ac}, ^6J_{ad}, ^6J_{ae}, ^5J_{af}: 0$	$^5J_{cf}$ 0.8
$^4J_{bc}, ^5J_{bd}, ^6J_{be}: 0$	$^3J_{de}$ 7.3
$^5J_{bf}$ 0.9	$^4J_{df}$ 0.9
$^3J_{cd}$ 7.9	$^3J_{ef}$ 8.4



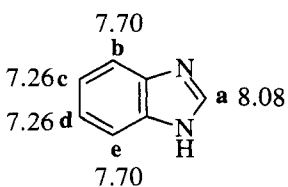
$^3J_{ab}$ 3.1	$^4J_{ce}$ 1.2
$^5J_{ac}, ^6J_{ad}, ^6J_{ae}, ^5J_{af}: 0$	$^5J_{cf}$ 0.9
$^3J_{ag}$ 2.5	$^5J_{cg}$ 0.8
$^4J_{bc}, ^5J_{bd}, ^6J_{be}: 0$	$^3J_{de}$ 7.1
$^5J_{bf}$ 0.7	$^4J_{df}$ 1.3
$^4J_{bg}$ 2.0	$^3J_{ef}$ 8.1
$^3J_{cd}$ 7.8	$^6J_{dg}, ^5J_{eg}, ^4J_{fg}: 0$



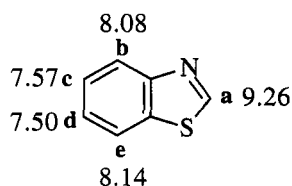
$^3J_{ab}$ 5.5	$^4J_{ce}$ 1.1
$^5J_{ac}, ^6J_{ad}, ^6J_{ae}, ^5J_{af}: 0$	$^5J_{cf}$ 0.9
$^4J_{bc}, ^5J_{bd}, ^6J_{be}: 0$	$^3J_{de}$ 7.2
$^5J_{bf}$ 0.8	$^4J_{df}$ 1.0
$^3J_{cd}$ 8.0	$^3J_{ef}$ 8.0



$^5J_{ab}$ 0.2	$^4J_{bd}$ 1.0
$^6J_{ac}$ -0.1	$^5J_{be}$ 0.7
$^6J_{ad}$ 0.4	$^3J_{cd}$ 7.4
$^5J_{ae}$ 0.0	$^4J_{ce}$ 1.2
$^3J_{bc}$ 8.2	$^3J_{de}$ 8.3

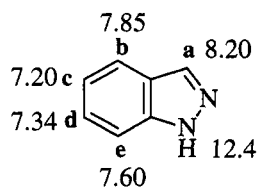


$^5J_{ab}, ^6J_{ac}, ^6J_{ad}, ^5J_{ae}: 0$	
$^3J_{bc}, ^3J_{de}$ 8.2	
$^4J_{bd}, ^4J_{ce}$ 1.4	
$^5J_{be}$ 0.7	
$^3J_{cd}$ 7.1	



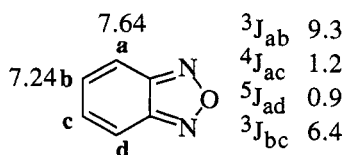
$^5J_{ab}$ 0.1
 $^6J_{ac}$ -0.2
 $^6J_{ad}$ 0.4
 $^5J_{ae}$ 0.1
 $^3J_{bc}$ 8.2

$^4J_{bd}$ 1.1
 $^5J_{be}$ 0.6
 $^3J_{cd}$ 7.2
 $^4J_{ce}$ 1.1
 $^3J_{de}$ 8.2

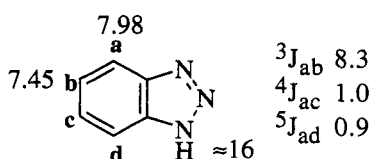


$^4J_{ab}, ^5J_{ac}, ^6J_{ad}$ 0
 $^5J_{ae}$ 0.8
 $^3J_{bc}$ 7.8
 $^4J_{bd}$ 1.2

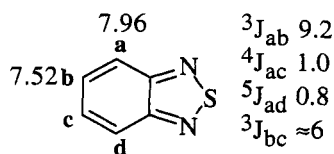
$^5J_{be}$ 1.0
 $^3J_{cd}$ 7.0
 $^4J_{ce}$ 1.2
 $^3J_{de}$ 7.9



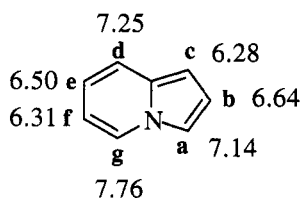
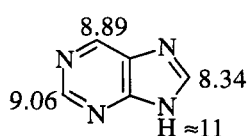
$^3J_{ab}$ 9.3
 $^4J_{ac}$ 1.2
 $^5J_{ad}$ 0.9
 $^3J_{bc}$ 6.4



$^3J_{ab}$ 8.3
 $^4J_{ac}$ 1.0
 $^5J_{ad}$ 0.9

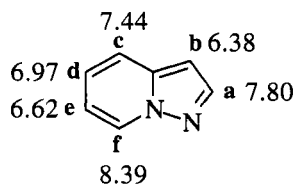


$^3J_{ab}$ 9.2
 $^4J_{ac}$ 1.0
 $^5J_{ad}$ 0.8
 $^3J_{bc}$ \approx 6



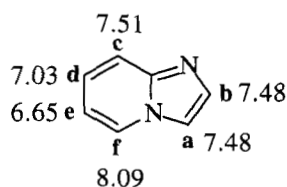
$^3J_{ab}$ 2.7
 $^4J_{ac}$ 1.2
 $^5J_{ad}$ 0.5
 $^6J_{ae}, ^5J_{af}, ^4J_{ag}$ 0
 $^3J_{bc}$ 3.9
 $^5J_{bd}, ^6J_{be}, ^5J_{bg}$ 0
 $^6J_{bf}$ 0.5
 $^4J_{cd}, ^5J_{ce}, ^6J_{cf}$ 0

$^5J_{cg}$ 1.0
 $^3J_{de}$ 9.0
 $^4J_{df}$ 1.0
 $^5J_{dg}$ 1.2
 $^3J_{ef}$ 6.4
 $^4J_{eg}$ 1.0
 $^3J_{fg}$ 6.8

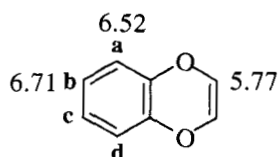


$^3J_{ab}$ 2.2
 $^5J_{ac}$ 0
 $^6J_{ad}$ 0.5
 $^6J_{ae}, ^5J_{af}$ 0
 $^4J_{bc}, ^5J_{bd}, ^6J_{be}$ 0
 $^5J_{bf}$ 0.9

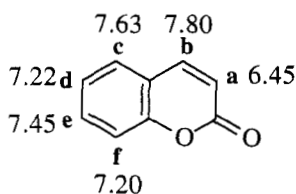
$^3J_{cd}$ 8.9
 $^4J_{ce}$ 1.2
 $^5J_{cf}$ 1.0
 $^3J_{de}$ 7.0
 $^4J_{df}$ 1.0
 $^3J_{ef}$ 6.9



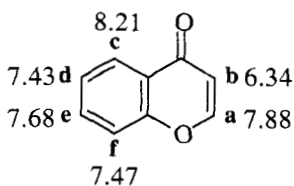
$^3J_{ab}$ 1.0	$^4J_{ce}$ 1.0
$^5J_{ac}, ^6J_{ad}, ^5J_{ae}$: 0	$^5J_{cf}$ 1.0
$^4J_{af}$ 0.7	$^3J_{de}$ 6.8
$^5J_{bc}, ^6J_{bd}, ^6J_{be}, ^5J_{bf}$: 0	$^4J_{df}$ 1.2
$^3J_{cd}$ 9.3	$^3J_{ef}$ 6.9



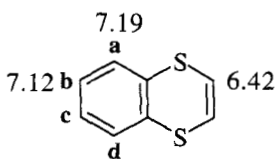
$^3J_{ab}$ 7.9
$^4J_{ac}$ 1.5
$^5J_{ad}$ 0.4
$^3J_{bc}$ 7.9



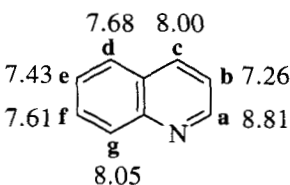
$^3J_{ab}$ 9.8	$^3J_{de}$ 8.6
$^3J_{cd}$ 8.5	$^4J_{df}$ 1.8
$^4J_{ce}$ 2.0	$^3J_{ef}$ 8.5
$^5J_{cf}$ 0.0	



$^3J_{ab}$ 6.1	$^3J_{de}$ 7.0
$^3J_{cd}$ 8.0	$^4J_{df}$ 1.1
$^4J_{ce}$ 1.8	$^3J_{ef}$ 8.4
$^5J_{cf}$ 0.5	

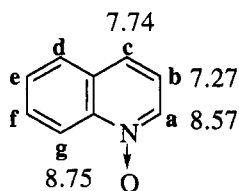


$^3J_{ab}$ 7.8
$^4J_{ac}$ 1.3
$^5J_{ad}$ 1.1
$^3J_{bc}$ 7.1



$^3J_{ab}$ 4.3	$^4J_{df}$ 1.6
$^4J_{ac}$ 1.8	$^5J_{dg}$ 0.5
$^3J_{bc}$ 8.3	$^3J_{ef}$ 6.8
$^5J_{cg}$ 0.8	$^4J_{eg}$ 1.1
$^3J_{de}$ 8.2	$^3J_{fg}$ 8.2

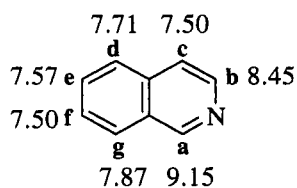




$^3J_{ab} = 6.0$

$^4J_{ac} = 1.1$

$^3J_{bc} = 8.5$



$^4J_{ab} = 0.8$

$^3J_{de} = 8.7$

$^5J_{ac} = 0$

$^4J_{df} = 1.1$

$^5J_{ad} < 0.5$

$^5J_{dg} = 0.9$

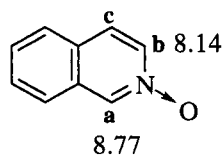
$^3J_{bc} = 6.0$

$^3J_{ef} = 7.0$

$^5J_{cg} = 0.8$

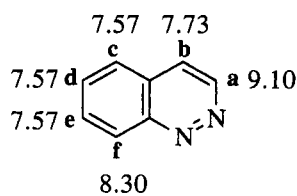
$^4J_{eg} = 1.3$

$^3J_{fg} = 8.2$



$^4J_{ab} = 1.7$

$^3J_{bc} = 7.0$



$^3J_{ab} = 5.7$

$^3J_{de} = 6.9$

$^5J_{bf} = 0.8$

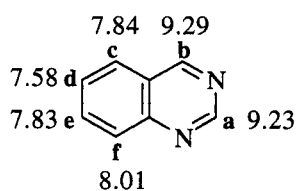
$^4J_{df} = 1.3$

$^3J_{cd} = 7.8$

$^3J_{ef} = 8.6$

$^4J_{ce} = 1.5$

$^5J_{cf} = 0.8$



$^4J_{ab} = 0$

$^3J_{de} = 6.9$

$^5J_{bf} = 0.5$

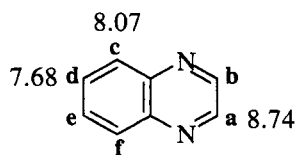
$^4J_{df} = 1.2$

$^3J_{cd} = 7.9$

$^3J_{ef} = 8.5$

$^4J_{ce} = 1.2$

$^5J_{cf} = 0.8$



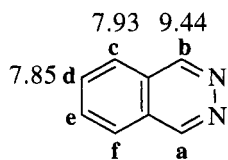
$^3J_{ab} = 1.8$

$^3J_{cd} = 8.4$

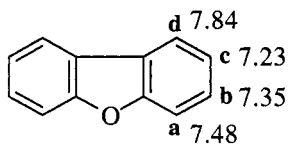
$^4J_{ce} = 1.6$

$^5J_{cf} = 0.6$

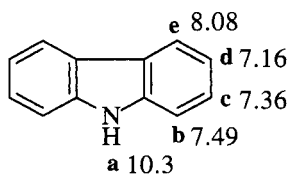
$^3J_{de} = 6.9$



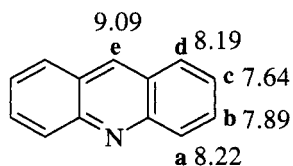
$^5J_{ac}$	0.4
$^3J_{cd}$	8.2
$^4J_{ce}$	1.2
$^5J_{cf}$	0.6
$^3J_{de}$	6.8



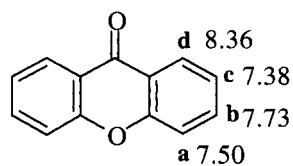
$^3J_{ab}$	8.5	$^3J_{bc}$	7.3
$^4J_{ac}$	0.9	$^4J_{bd}$	1.3
$^5J_{ad}$	0.6	$^3J_{cd}$	7.6



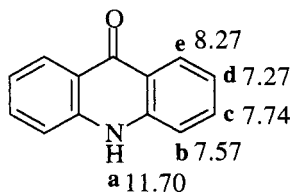
$^5J_{ae}$	0.7	$^3J_{cd}$	7.2
$^3J_{bc}$	8.2	$^4J_{ce}$	1.2
$^4J_{bd}$	0.9	$^3J_{de}$	7.8
$^5J_{be}$	0.7		



$^3J_{ab}$	9.0	$^3J_{bc}$	6.6
$^4J_{ac}$	1.2	$^4J_{bd}$	1.4
$^5J_{ad}$	0.6	$^3J_{cd}$	8.2
$^5J_{ae}$	0.9	$^4J_{de}$	0.4



$^3J_{ab}$	8.4	$^3J_{bc}$	7.1
$^4J_{ac}$	1.1	$^4J_{bd}$	1.8
$^5J_{ad}$	0.5	$^3J_{cd}$	8.0



$^5J_{ae}$	0.4	$^3J_{cd}$	7.0
$^3J_{bc}$	8.6	$^4J_{ce}$	1.4
$^4J_{bd}$	1.0	$^3J_{de}$	8.2
$^5J_{be}$	0.4		



5.7

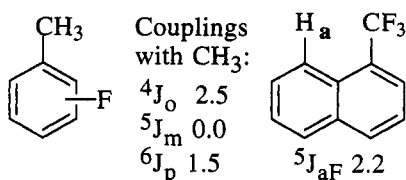
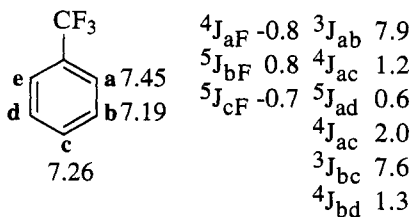
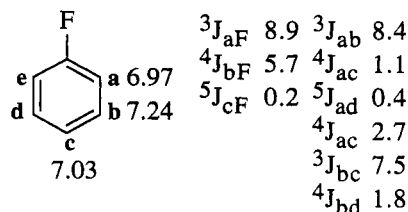
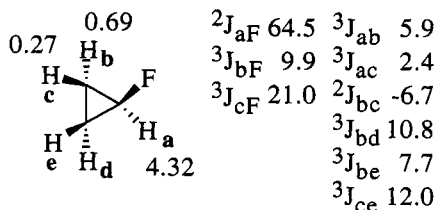
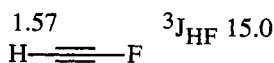
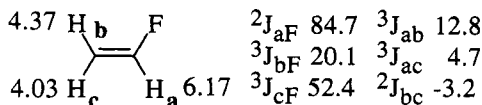
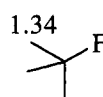
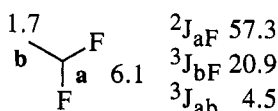
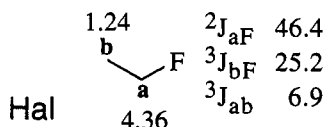
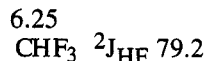
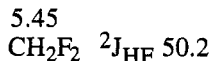
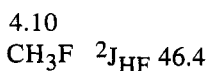
Halogen Compounds

5.7.1

Fluoro Compounds

Fluorine in nature occurs 100% as ^{19}F , which exhibits a spin quantum number $I = 1/2$. The signals of ^1H atoms are split by coupling to ^{19}F up to a distance of about four bonds.

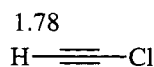
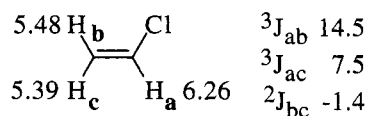
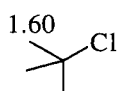
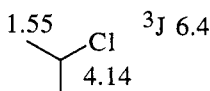
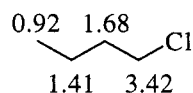
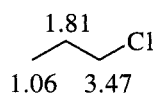
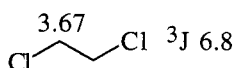
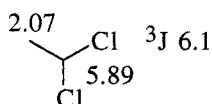
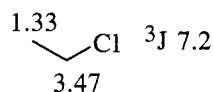
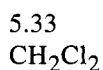
^1H Chemical Shifts and Coupling Constants of Fluoro Compounds (δ in ppm relative to TMS, J in Hz)



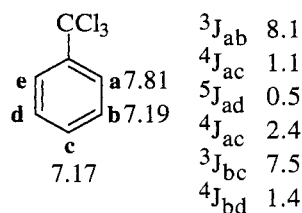
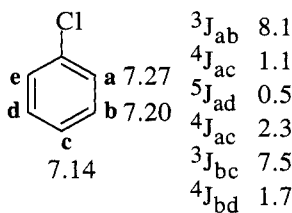
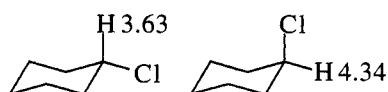
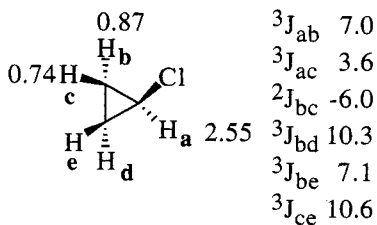
5.7.2

Chloro Compounds

¹H Chemical Shifts and Coupling Constants of Chloro Compounds (δ in ppm relative to TMS, J in Hz)



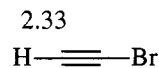
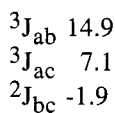
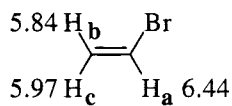
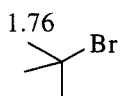
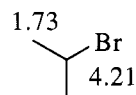
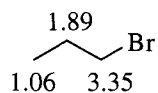
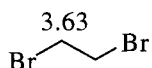
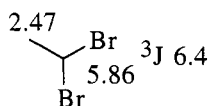
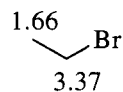
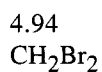
Hal



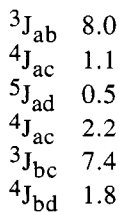
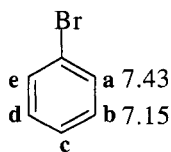
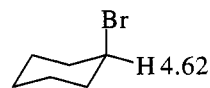
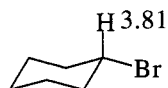
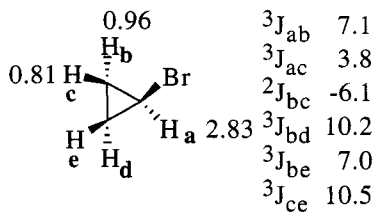
5.7.3

Bromo Compounds

^1H Chemical Shifts and Coupling Constants of Bromo Compounds (δ in ppm relative to TMS, J in Hz)



Hal



5.7.4 Iodo Compounds

¹H Chemical Shifts and Coupling Constants of Iodo Compounds
(δ in ppm relative to TMS, J in Hz)

2.16

CH₃I

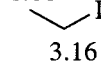
3.90

CH₂I₂

4.91

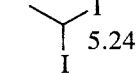
CHI₃

1.88



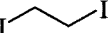
3.16

2.96

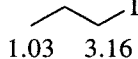
³J 7.0

5.24

3.70



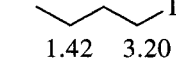
1.88



1.03

3.16

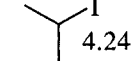
0.93



1.42

3.20

1.89

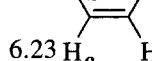
³J 7.0

4.24

1.95

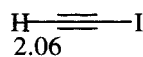


6.57



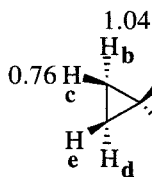
6.23

6.53

H_bH_cH_a³J_{ab} 15.9³J_{ac} 7.8²J_{bc} -1.5

2.06

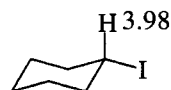
Hal



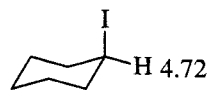
1.04

0.76

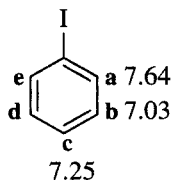
2.31

³J_{ab} 7.5³J_{ac} 4.4²J_{bc} -5.9³J_{bd} 9.9³J_{be} 6.6³J_{ce} 10.0

H 3.98



I 4.72



I

a 7.64

b 7.03

c 7.25

³J_{ab} 7.9⁴J_{ac} 1.1⁵J_{ad} 0.5⁴J_{ac} 1.9³J_{bc} 7.5⁴J_{bd} 1.8

5.8

Alcohols, Ethers, and Related Compounds

5.8.1

Alcohols

 *^1H Chemical Shifts and Coupling Constants of Alcohols**(δ in ppm relative to TMS, J in Hz)*

Aliphatic and alicyclic alcohols: 0.5–3.0 (in DMSO: 4–6)

Phenols: 4.0–8.0 (in DMSO: 8–12)

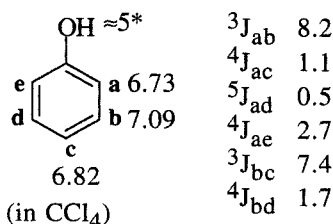
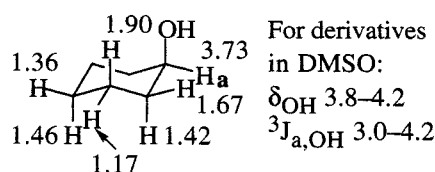
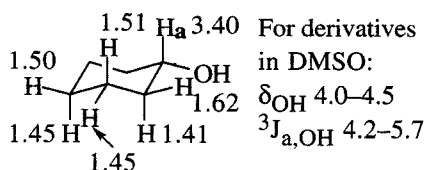
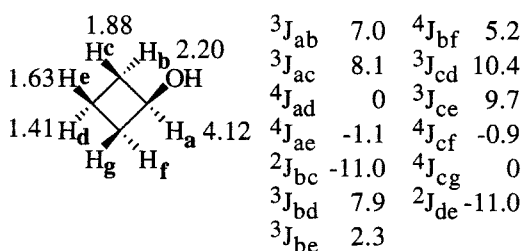
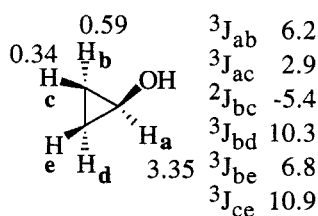
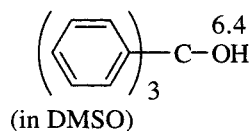
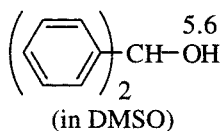
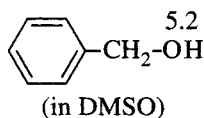
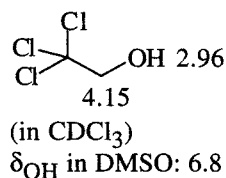
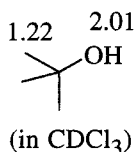
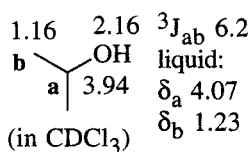
Hydrogen bonds strongly deshield hydroxyl protons. The position of the signal may depend heavily on the experimental conditions. If a compound contains several kinds of hydroxyl protons ($-\text{OH}$, $-\text{COOH}$, H_2O), in general only one signal at an average position is observed because of rapid exchange. In dimethyl sulfoxide (DMSO) as solvent, this exchange in most cases is so slow that isolated signals are observed. In this case, the chemical shifts of hydroxyl protons are characteristic. However, if the sample contains strong acids or amine bases, the exchange rate increases, and also in DMSO, a signal at an average position is observed. Frequently, intermediate exchange rates lead to very broad signals extending over several ppm and, therefore, sometimes not discernible in routine spectra.

As a consequence of fast intermolecular exchange of the hydroxyl protons, their coupling with the protons on the adjacent carbon atoms is usually not observed. However, in very pure (acid-free) solutions or in DMSO, the exchange is sufficiently slow so that the $\text{H}-\text{O}-\text{C}-\text{H}$ couplings become visible. Their dependence on the conformation is analogous to that shown by the $\text{H}-\text{C}-\text{C}-\text{H}$ couplings (Chapter 5.1). In case of fast rotation: $^3J_{\text{HOCH}} \approx 5$ Hz. In cyclohexanols, the vicinal coupling constants for axial hydroxyl protons (3.0–4.2 Hz) are lower than those of equatorial ones (4.2–5.7 Hz).

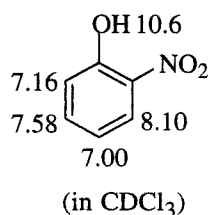
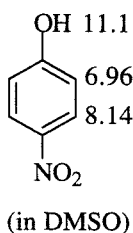
3.39 3.9 in DMSO:
 CH_3OH_a $^3J_{ab}$ 5.2
 b
 (in CDCl_3)

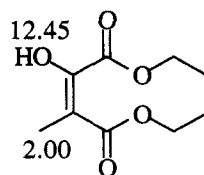
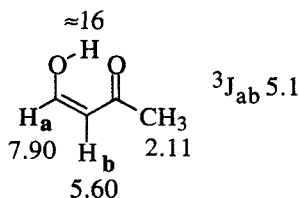
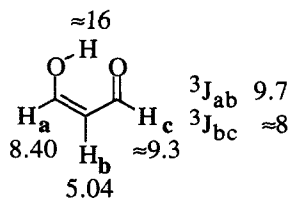
1.18 2.61 liquid: in DMSO:
 $\text{c} \text{---} \text{b} \text{---} \text{OH}_a$ δ_a 5.27 δ_a 4.5
 δ_b 3.66
 δ_c 1.19
 (in CDCl_3) $^3J_{ab}$ 4.8
 $^3J_{bc}$ 6.9

1.53 2.26
 $\text{c} \text{---} \text{b} \text{---} \text{OH}$
 δ_c 0.93 δ_b 3.49
 (in CDCl_3)

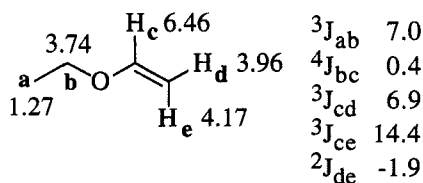
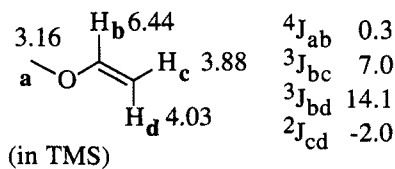
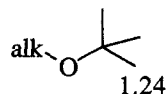
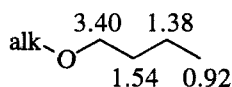
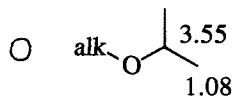
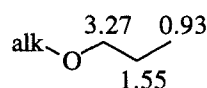
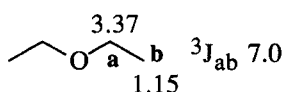
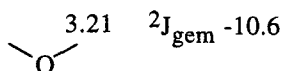
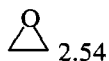


* in DMSO: δ_{OH} 9.3



^1H Chemical Shifts of Enols (δ in ppm relative to TMS, J in Hz)

(in CDCl_3 , partly enolized)

5.8.2 Ethers **^1H Chemical Shifts and Coupling Constants of Ethers** (δ in ppm relative to TMS, J in Hz) **^1H Chemical Shifts and Coupling Constants of Cyclic Ethers** (δ in ppm relative to TMS, J in Hz)

In derivatives:

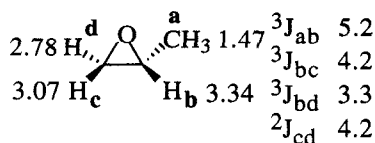
$^2J_{\text{gem}}$ 5-6

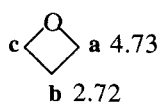
$^3J_{\text{cis}}$ 4.5

$^3J_{\text{trans}}$ 3.1

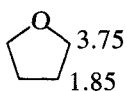
Throughout:

$J_{\text{cis}} > J_{\text{trans}}$

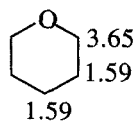




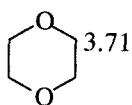
$^2J_{a,gem}$	-5.8
$^2J_{b,gem}$	-11.0
$^3J_{cis}$	8.7
$^3J_{trans}$	6.6
$^3J_{ac}$	<0.3



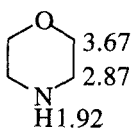
3.75
1.85



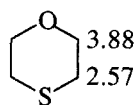
3.65
1.59



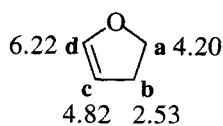
3.71



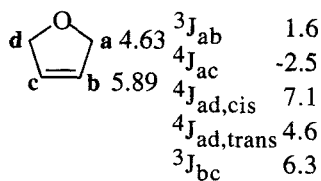
3.67
2.87
H 1.92



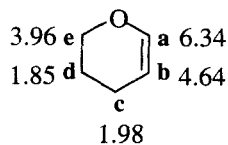
3.88
2.57



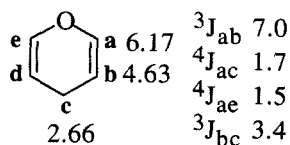
6.22 d	a 4.20	$^3J_{ab,cis}$	8.3
c	b	$^3J_{ab,trans}$	10.7
4.82	2.53	$^3J_{bc}$	2.5
		$^4J_{bd}$	2.6
		$^3J_{cd}$	2.6



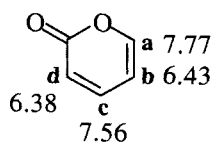
d	a 4.63	$^3J_{ab}$	1.6
c	b 5.89	$^4J_{ac}$	-2.5
		$^4J_{ad,cis}$	7.1
		$^4J_{ad,trans}$	4.6
		$^3J_{bc}$	6.3



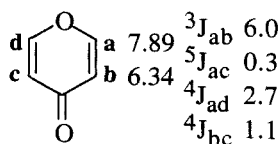
3.96 e	a 6.34	$^3J_{ab}$	6.2
1.85 d	b 4.64	$^4J_{ac}$	2.0
c		$^3J_{bc}$	3.8
1.98		$^4J_{bd}$	0.6



e	a 6.17	$^3J_{ab}$	7.0
d	b 4.63	$^4J_{ac}$	1.7
c		$^4J_{ae}$	1.5
2.66		$^3J_{bc}$	3.4

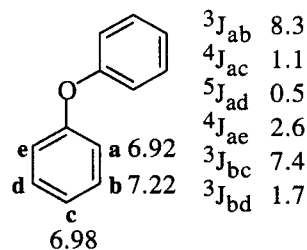
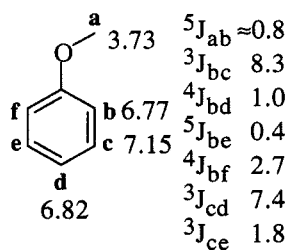


d	a 7.77	$^3J_{ab}$	5.0
c	b 6.43	$^4J_{ac}$	2.4
6.38		$^5J_{ad}$	1.2
7.56		$^3J_{bc}$	6.3
		$^4J_{bd}$	1.5
		$^3J_{cd}$	9.4

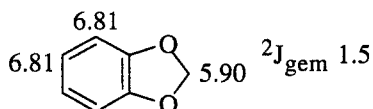
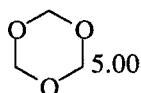
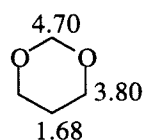
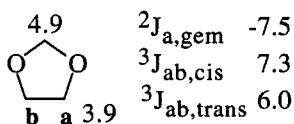
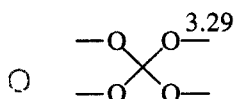
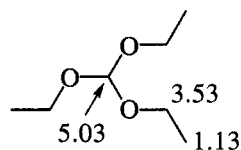
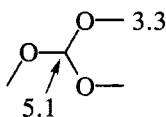
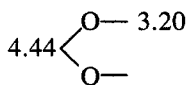


d	a 7.89	$^3J_{ab}$	6.0
c	b 6.34	$^5J_{ac}$	0.3
		$^4J_{ad}$	2.7
		$^4J_{bc}$	1.1

^1H Chemical Shifts and Coupling Constants of Aromatic Ethers
 (δ in ppm relative to TMS, J in Hz)



^1H Chemical Shifts and Coupling Constants of Acetals, Ketals, and Ortho Esters
 (δ in ppm relative to TMS, J in Hz)

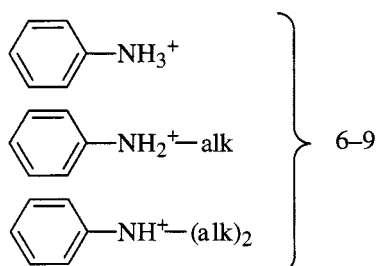
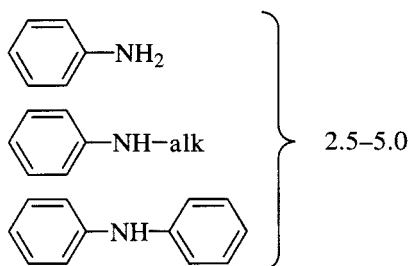
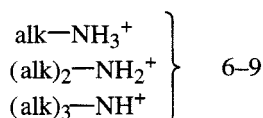
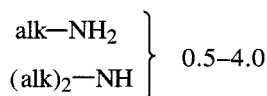


5.9 Nitrogen Compounds

5.9.1 Amines

Amine and Ammonium Protons (δ in ppm relative to TMS, $|J|$ in Hz)

Chemical shifts of amine protons lie around 0.5–5 ppm depending on solvent, concentration, and hydrogen bonding. Those of ammonium protons are found between ca. 6 and 9 ppm:



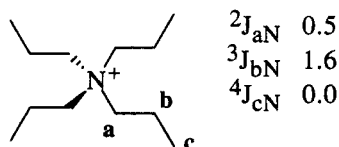
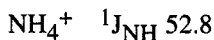
N

Coupling of amine protons with vicinal H atoms is usually not seen in aliphatic amines because of their rapid intermolecular exchange. However, for $=\text{C}-\text{NH}-\text{CH}$ moieties (enamines, aromatic amines, amides, etc.), the exchange rate is slower and splitting is often observed. The $\text{H}-\text{C}-\text{N}-\text{H}$ coupling depends on the conformation in a similar way as the $\text{H}-\text{C}-\text{C}-\text{H}$ coupling (see Chapter 5.1). For $\text{N}-\text{CH}_3$ and $\text{N}-\text{CH}_2$ groups: $^3J_{\text{HCNH}} \approx 5-6$.

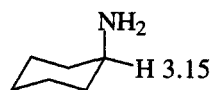
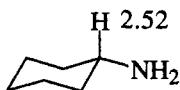
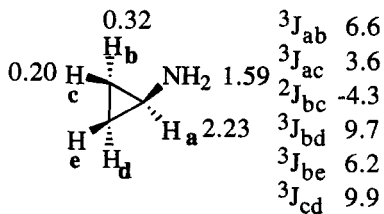
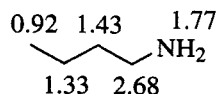
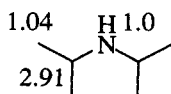
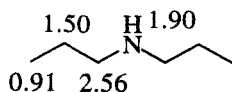
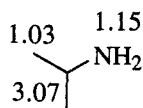
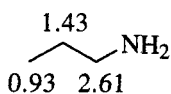
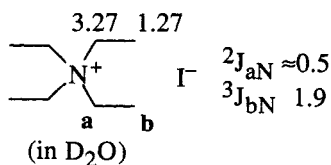
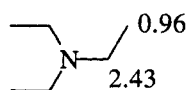
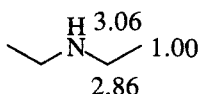
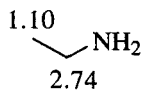
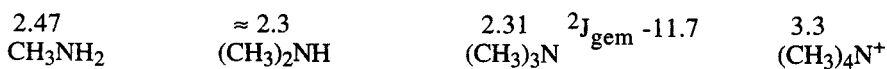
In acidic media (e.g., in trifluoroacetic acid as solvent), the exchange of the *ammonium* protons is slowed down to such an extent that the vicinal coupling $\text{H}-\text{N}^+-\text{C}-\text{H}$ generally becomes observable. In other media, signals are usually broad owing to intermediate exchange rates.

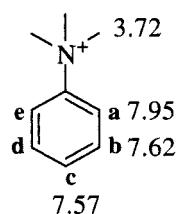
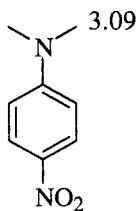
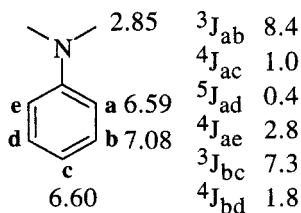
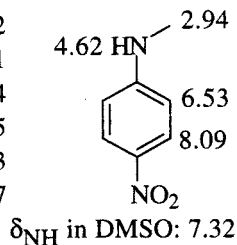
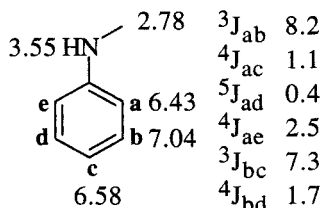
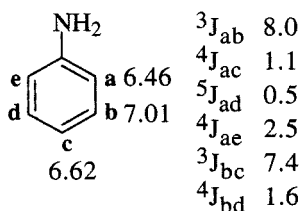
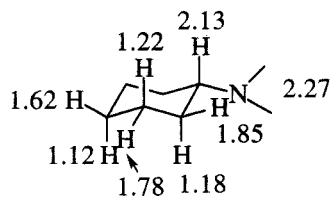
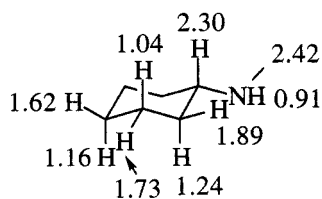
The signals of amine and especially of ammonium protons are often broadened additionally because the $^{14}\text{N}-^1\text{H}$ coupling is only partly eliminated by the quadrupole relaxation of ^{14}N (spin quantum number, $I = 1$; natural abundance, 99.6 %; $^1J_{\text{NH}} \approx 60$). This line broadening has no effect on the vicinal $\text{H}-\text{C}-\text{N}-\text{H}$ coupling so that sharp multiplets can be observed for neighboring H atoms. In

ammonium compounds of high symmetry, the quadrupole relaxation is slow and the coupling with ^{14}N leads to triplets of equal intensity for all three lines.



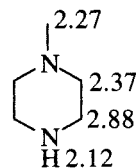
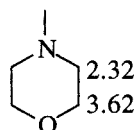
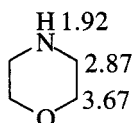
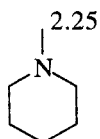
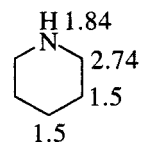
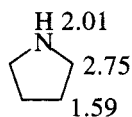
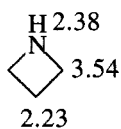
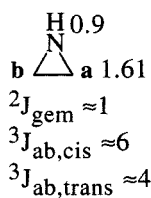
^1H Chemical Shifts and Coupling Constants of Amines
 (δ in ppm relative to TMS, J in Hz)





¹H Chemical Shifts and Coupling Constants of Cyclic Amines
(δ in ppm relative to TMS, J in Hz)

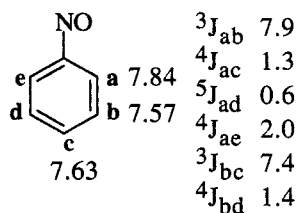
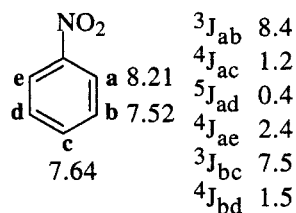
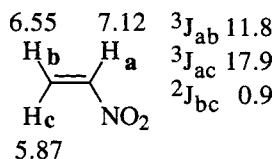
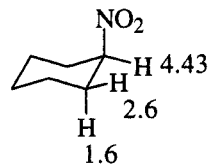
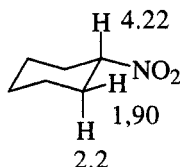
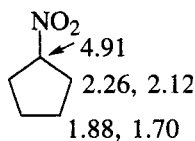
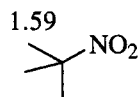
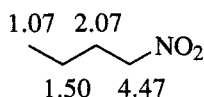
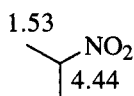
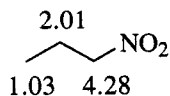
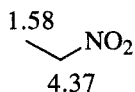
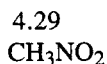
N



5.9.2

Nitro and Nitroso Compounds

^1H Chemical Shifts and Coupling Constants of Nitro and Nitroso Compounds (δ in ppm relative to TMS, J in Hz)



N

5.9.3

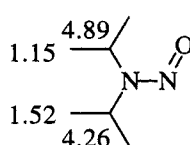
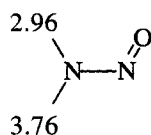
Nitrosamines, Azo and Azoxy Compounds

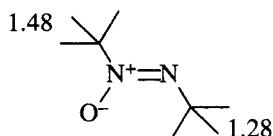
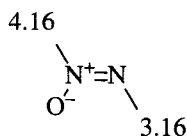
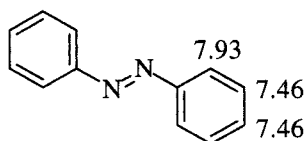
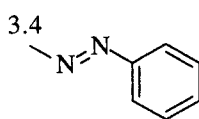
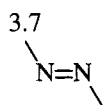
^1H Chemical Shifts of Nitrosamines, Azo and Azoxy Compounds (δ in ppm relative to TMS)

Generally:

$\delta_{\text{cis}} < \delta_{\text{trans}}$ for $\alpha\text{-CH}_3$, $\alpha\text{-CH}_2$, and $\beta\text{-CH}_3$ protons

$\delta_{\text{cis}} > \delta_{\text{trans}}$ for $\alpha\text{-CH}$ protons

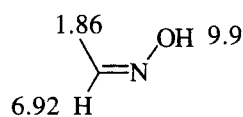
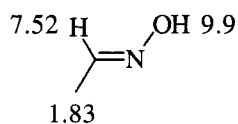
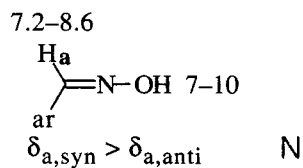
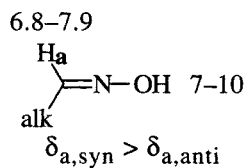
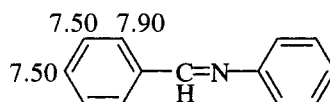
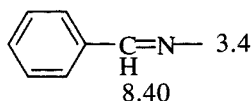




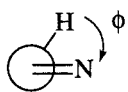
5.9.4

Imines, Oximes, Hydrazones, and Azines

¹H Chemical Shifts and Coupling Constants of Imines, Oximes, Hydrazones, and Azines (δ in ppm relative to TMS)

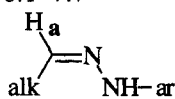


In aldoximes and ketoximes, the chemical shift difference between *syn* and *anti* protons at the α -CH groups, $\Delta\delta = \delta_{syn} - \delta_{anti}$, depends on the dihedral angle, $\phi_{H-C-C=N}$:

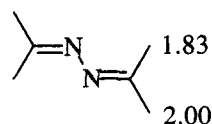
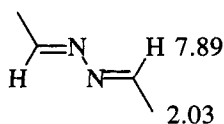


ϕ	$\Delta\delta$
0°	1
60°	0
115°	-0.3

6.1–7.7

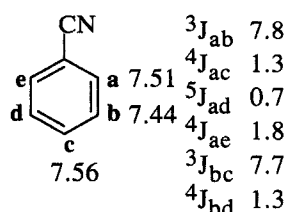
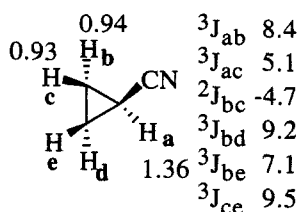
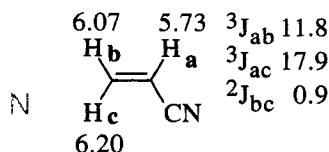
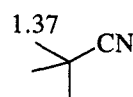
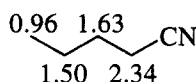
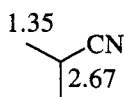
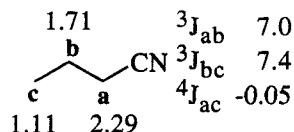
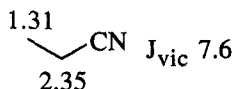


$$\delta_{a,\text{syn}} > \delta_{a,\text{anti}}$$

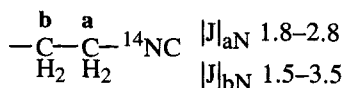


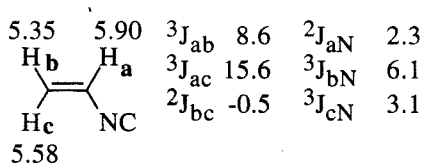
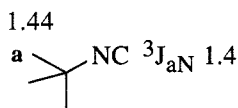
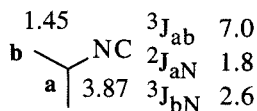
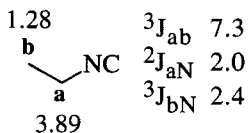
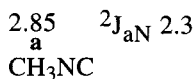
5.9.5

Nitriles and Isonitriles

 ^1H Chemical Shifts and Coupling Constants of Nitriles(δ in ppm relative to TMS, J in Hz) ^1H Chemical Shifts and Coupling Constants of Isonitriles(δ in ppm relative to TMS, J in Hz)

Because of the symmetrical electron distribution around the N atom, the quadrupole relaxation of the nitrogen nucleus is so slow that the ^{14}N - ^1H coupling becomes observable and leads to triplets with relative intensities of 1:1:1 (spin quantum number of ^{14}N : $I = 1$; natural abundance, 99.6 %):

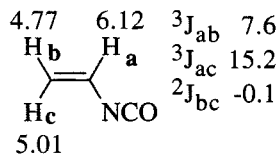
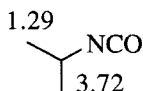
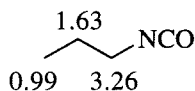
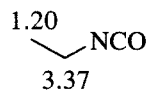
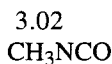
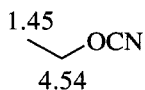




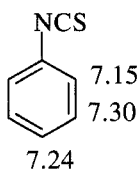
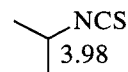
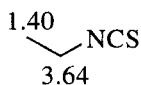
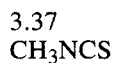
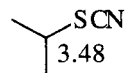
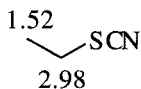
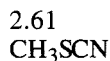
5.9.6

Cyanates, Isocyanates, Thiocyanates, and Isothiocyanates

¹H Chemical Shifts and Coupling Constants of Cyanates, Isocyanates, Thiocyanates, and Isothiocyanates
 (δ in ppm relative to TMS, J in Hz)



N



5.10

Sulfur-Containing Functional Groups

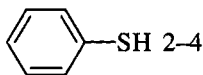
5.10.1

Thiols

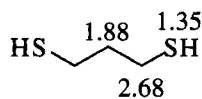
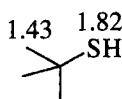
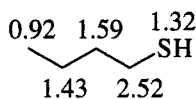
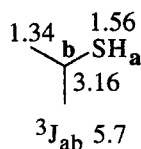
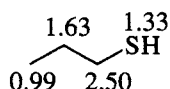
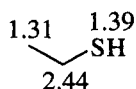
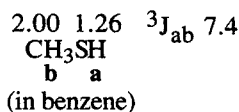
^1H Chemical Shifts and Coupling Constants of Thiols
 (δ in ppm relative to TMS, J in Hz)

Typical ranges of SH chemical shifts:

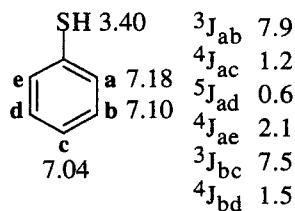
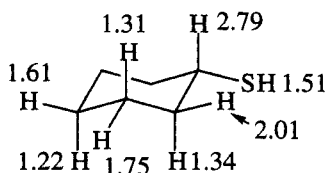
alk-SH 1-2



The exchange with other SH, OH, NH, or COOH protons is generally so slow that the chemical shift is characteristic and the vicinal coupling with SH protons becomes visible (5-9 Hz in aliphatic systems with fast rotation).

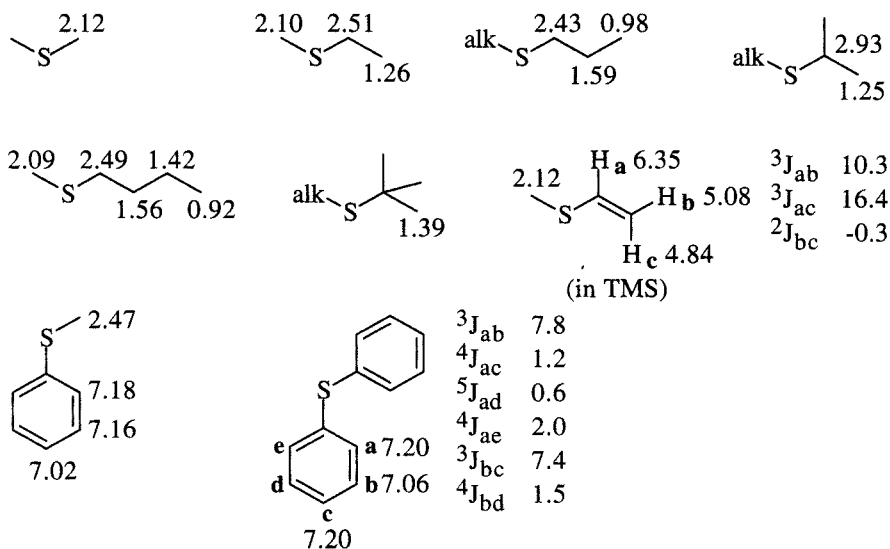


S

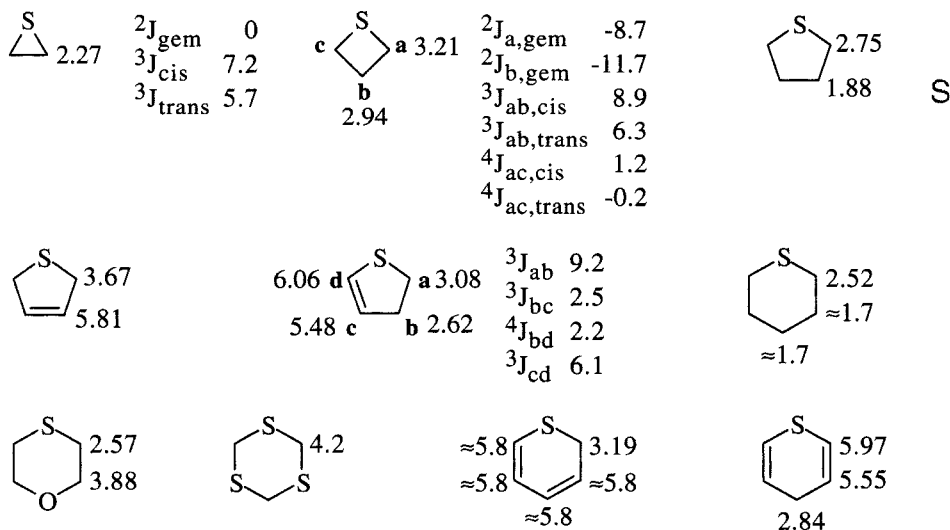


5.10.2 Sulfides

¹H Chemical Shifts and Coupling Constants of Sulfides (δ in ppm relative to TMS, J in Hz)



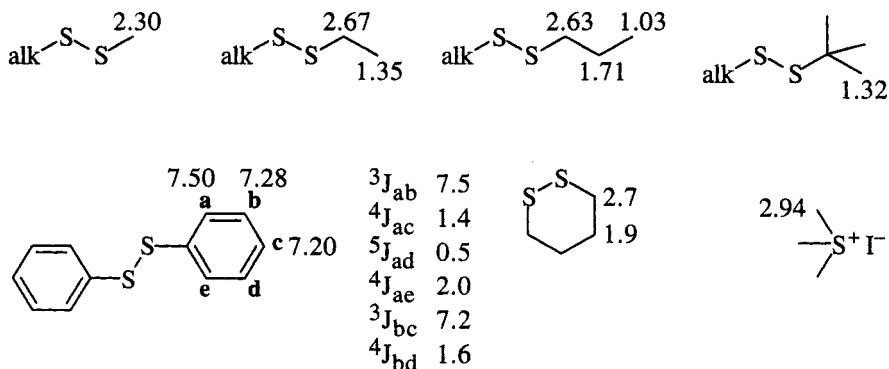
¹H Chemical Shifts and Coupling Constants of Cyclic Sulfides (δ in ppm relative to TMS, J in Hz)



5.10.3

Disulfides and Sulfonium Salts

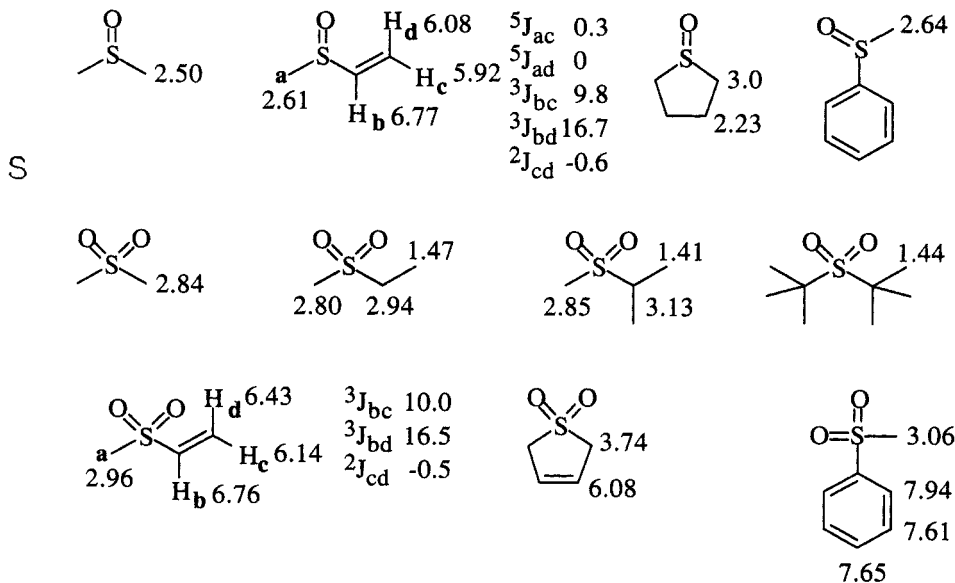
^1H Chemical Shifts and Coupling Constants of Disulfides and Sulfonium Salts (δ in ppm relative to TMS, J in Hz)



5.10.4

Sulfoxides and Sulfones

^1H Chemical Shifts and Coupling Constants of Sulfoxides and Sulfones (δ in ppm relative to TMS, J in Hz)



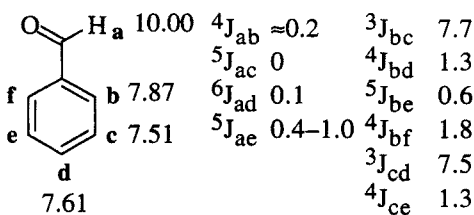
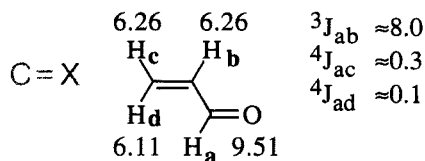
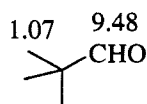
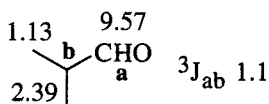
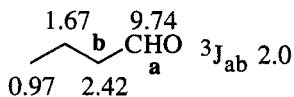
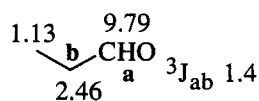
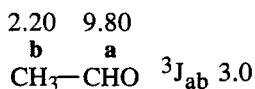
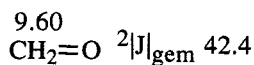
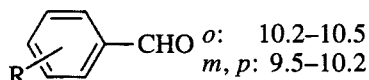
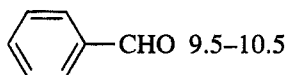
5.11 Carbonyl Compounds

5.11.1 Aldehydes

^1H Chemical Shifts and Coupling Constants of Aldehydes
(δ in ppm relative to TMS, J in Hz)

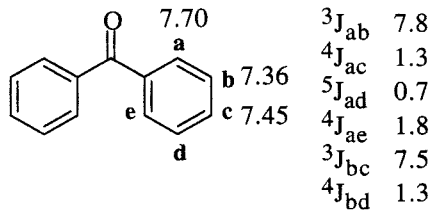
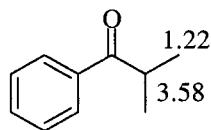
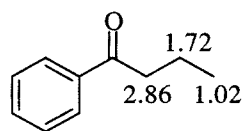
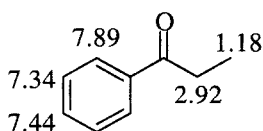
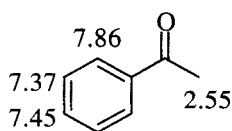
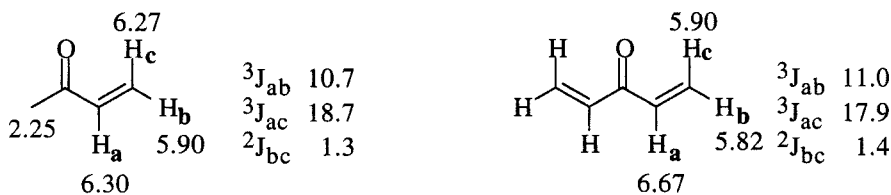
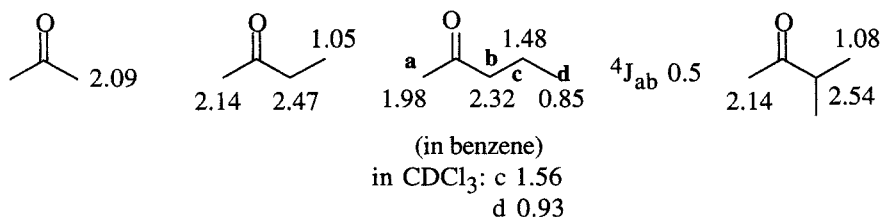
Typical ranges for chemical shifts and coupling constants of aldehyde protons:

alk-CHO 9.0–10.1 $^3J_{\text{vic}}$ 0–3 alken-CHO 9.0–10.1 $^3J_{\text{vic}} \approx 8$

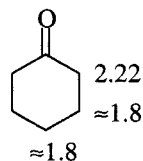
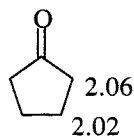
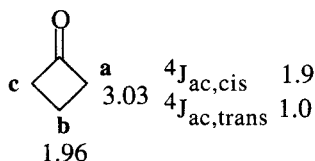
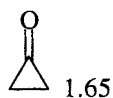


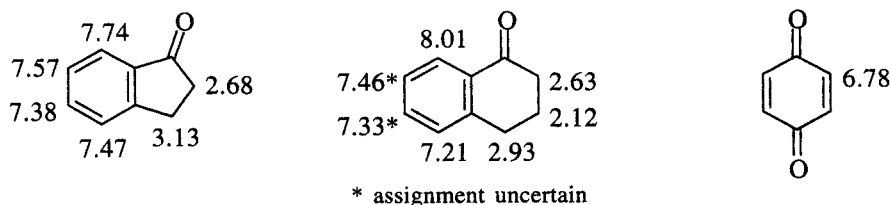
5.11.2 Ketones

¹H Chemical Shifts and Coupling Constants of Ketones
(δ in ppm relative to TMS, J in Hz)

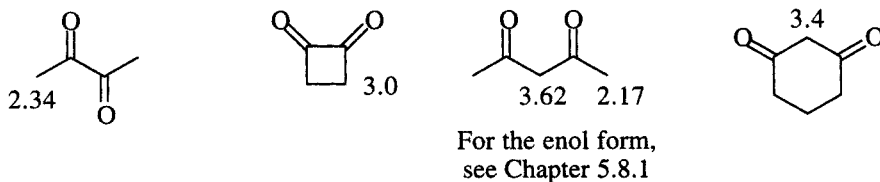


C=X





^1H Chemical Shifts of Diketones (δ in ppm relative to TMS)



Long-Range Coupling in Ketones ($|J|$ in Hz)

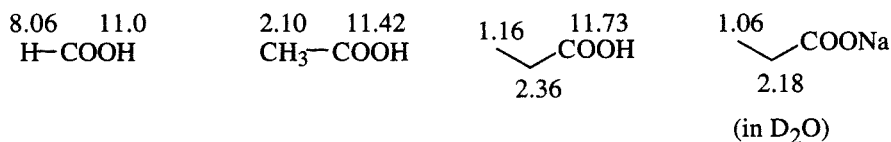
Coupling over the $\text{C}=\text{O}$ group is often detectable for fixed conformations in W-arrangement of the coupling path:

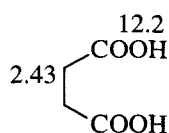
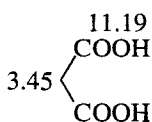
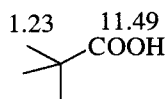
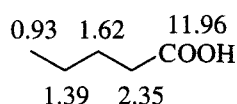
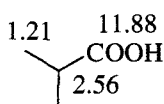
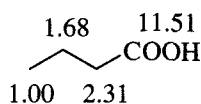


5.11.3 Carboxylic Acids and Carboxylates

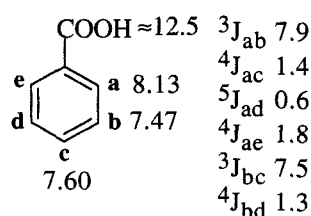
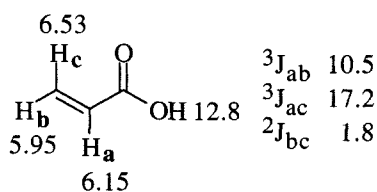
^1H Chemical Shifts of Carboxyl Protons (δ in ppm relative to TMS, J in Hz)

The position of the COOH signal depends on the solvent, the concentration, and the presence of other exchangeable protons. Intermediate rates of exchange with other protons may induce very broad lines, which are sometimes not even detected.



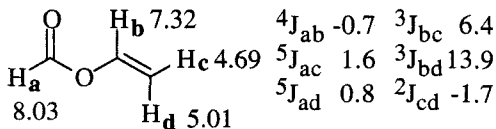
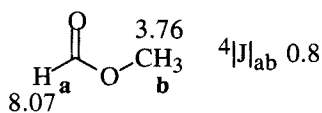


(in DMSO)

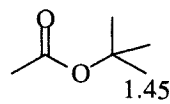
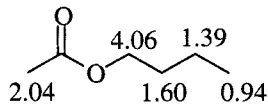
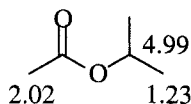
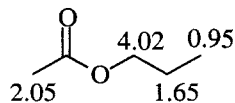
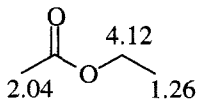
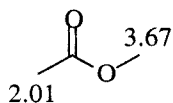


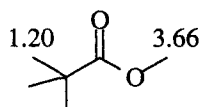
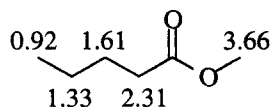
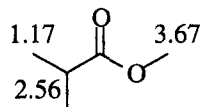
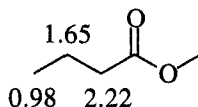
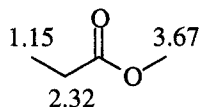
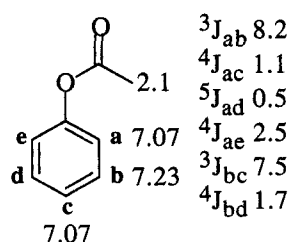
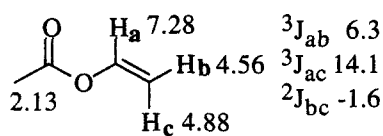
5.11.4 Esters and Lactones

¹H Chemical Shifts and Coupling Constants of Aliphatic Carboxylic Acid Esters (δ in ppm relative to TMS, J in Hz)



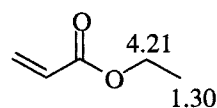
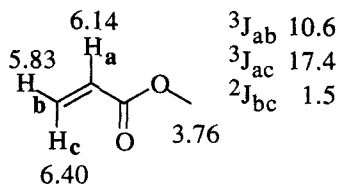
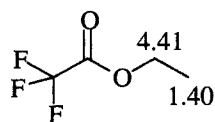
C=X



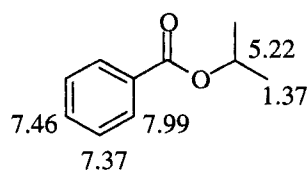
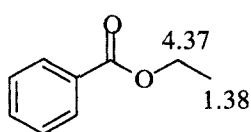
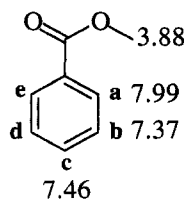


For esters of boronic, nitric, and sulfuric acid, see Chapter 5.12.

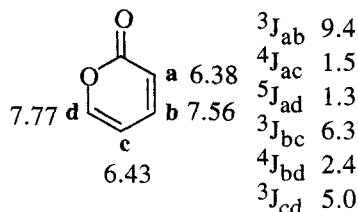
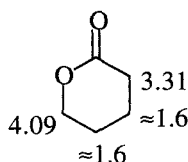
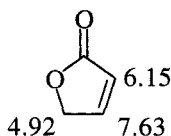
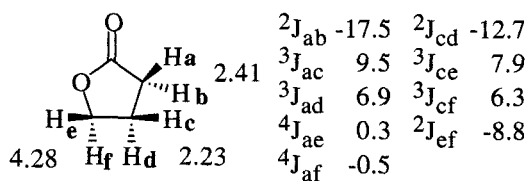
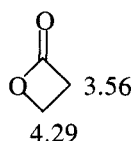
^1H Chemical Shifts and Coupling Constants of Alkyl Esters
(δ in ppm relative to TMS)



$\text{C}=\text{X}$

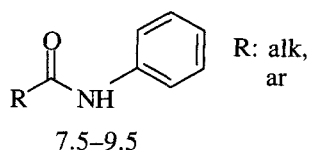
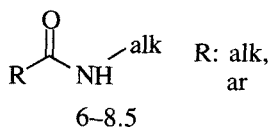
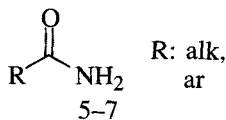


^1H Chemical Shifts and Coupling Constants of Lactones
 (δ in ppm relative to TMS, J in Hz)



5.11.5 Amides and Lactams

Amide Protons (δ in ppm relative to TMS, J in Hz)



Line Widths

The signals of the NH protons are often broad because the ^{14}N - ^1H coupling is only partly eliminated by the quadrupole relaxation of ^{14}N (spin quantum number, $I = 1$; $^1J_{\text{NH}} \approx 60$). In primary amides, the hindered rotation around the CO-N bond is another reason for line broadening. At slow rotation, the chemical shifts of the two primary amide protons differ by about 0.5-1 ppm.

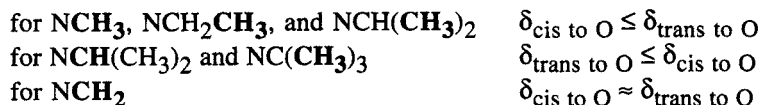
C = X

Vicinal Coupling H-C-N-H

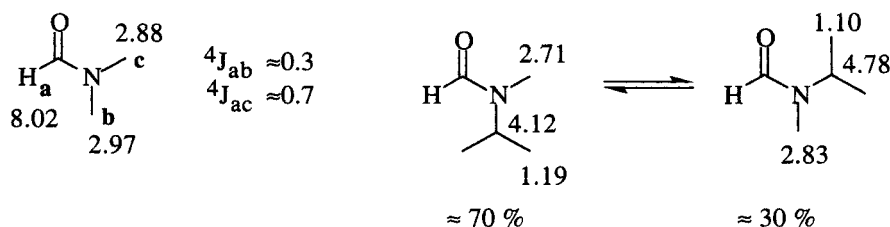
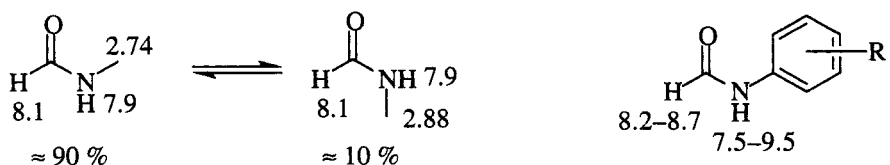
Due to the slow intermolecular exchange of amide protons, their coupling to neighboring hydrogen atoms is usually detectable. The splitting of the C-H signal is clearly observed even in those cases where the signal of the NH proton is broad and featureless. The H-C-N-H coupling depends on the conformation in a similar way as the H-C-C-H coupling (see Chapter 5.1). For N-CH₃ and N-CH₂ groups: $^3J_{\text{HCNH}} \approx 7$.

Tertiary Alkylamides

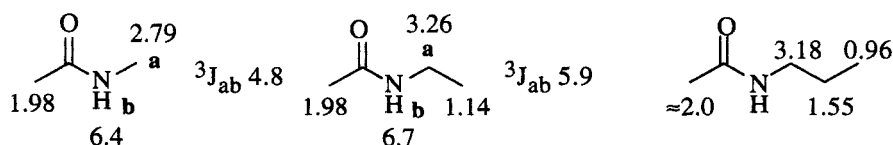
The rotation around the CO-N bond is usually so slow that, with different N-substituents, two separate signals are observed for the two conformers. In general, the following relationships hold:

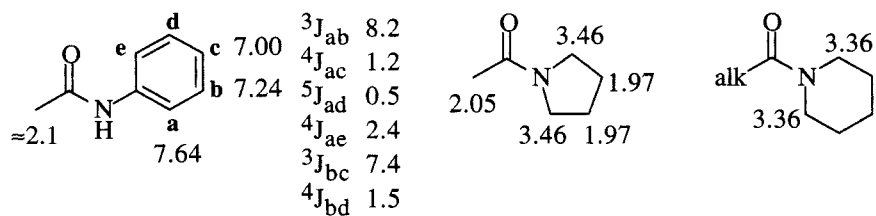
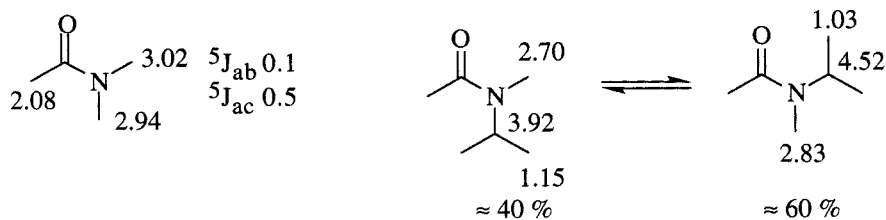
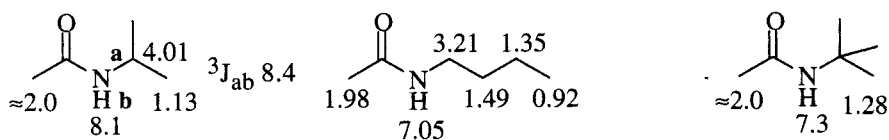
**Formamides** (δ in ppm relative to TMS, $|J|$ in Hz)

In the more stable conformer of *monosubstituted* formamides, the substituent occupies the *cis* position relative to the carbonyl oxygen. In the more stable conformer of asymmetrically *disubstituted* formamides, the larger substituent occupies the *trans* position relative to the carbonyl oxygen.

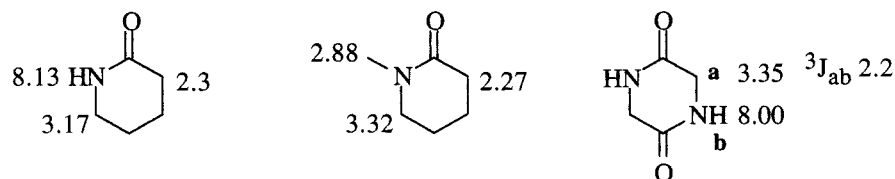
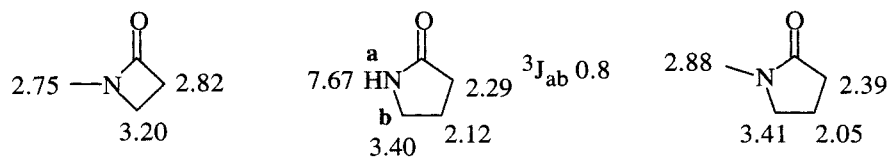
**Acetamides** (δ in ppm relative to TMS, J in Hz)

$\text{C}=\text{X}$ In *monosubstituted* acetamides, the substituent of the only observable conformer is *cis* to the carbonyl oxygen. In *disubstituted* acetamides, the more stable conformer has the larger substituent *cis* to the carbonyl oxygen.





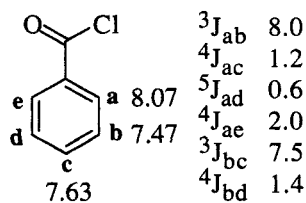
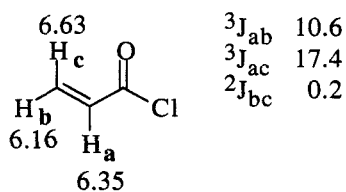
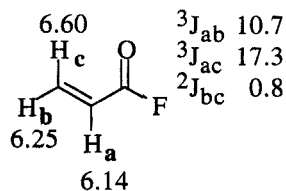
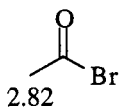
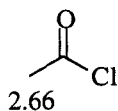
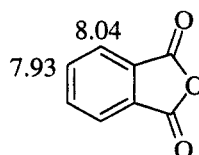
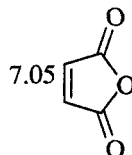
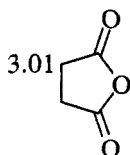
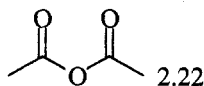
¹H Chemical Shifts of Lactams (δ in ppm relative to TMS)



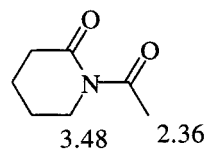
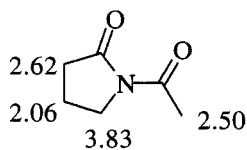
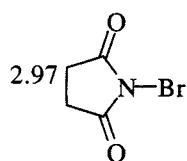
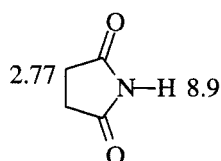
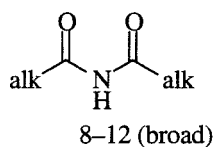
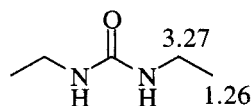
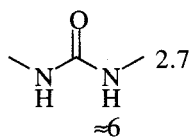
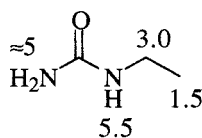
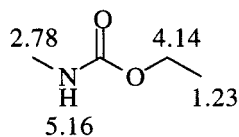
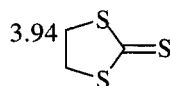
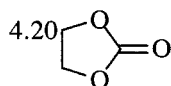
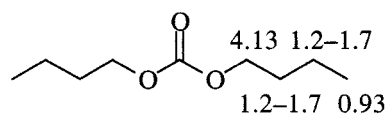
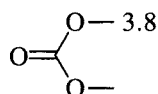
C = X

5.11.6

Miscellaneous Carbonyl Derivatives

 ^1H Chemical Shifts of Carboxylic Acid Halides(δ in ppm relative to TMS, J in Hz) ^1H Chemical Shifts of Carboxylic Acid Anhydrides(δ in ppm relative to TMS)

C=X

¹H Chemical Shifts of Carboxylic Acid Imides*(δ in ppm relative to TMS)****¹H Chemical Shifts of Carbonic Acid Derivatives****(δ in ppm relative to TMS)***C=X**

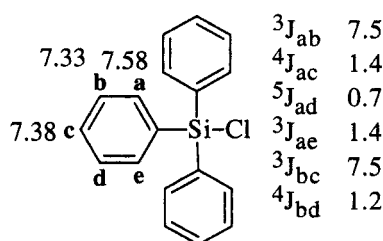
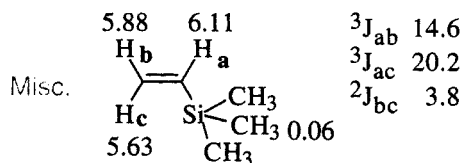
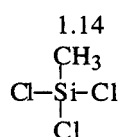
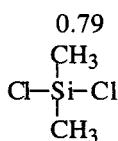
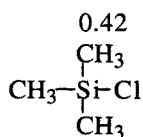
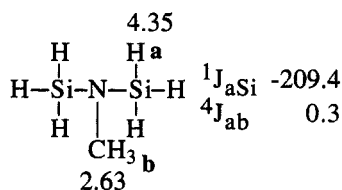
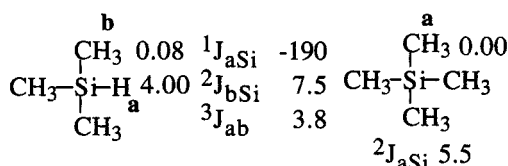
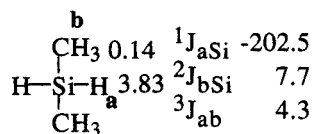
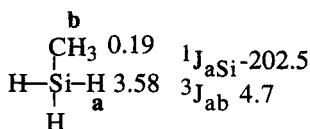
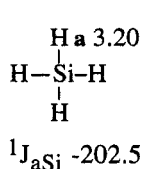
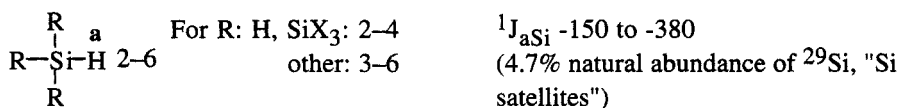
5.12

Miscellaneous Compounds

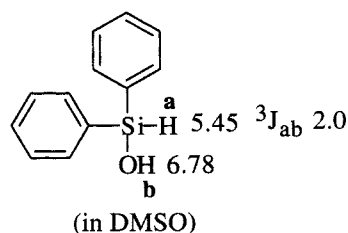
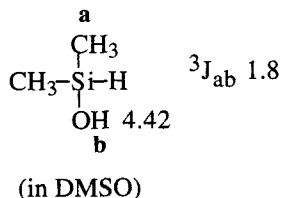
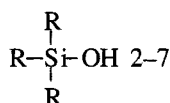
5.12.1

Silicon Compounds

^1H Chemical Shifts and Coupling Constants of Silanes and Silanols (δ in ppm relative to TMS, J in Hz)



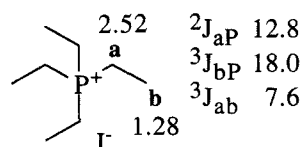
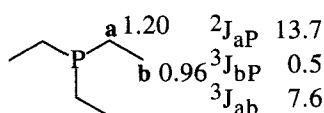
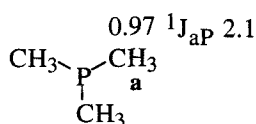
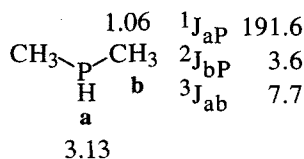
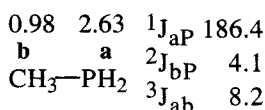
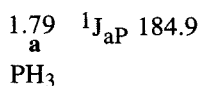
The silanol hydrogen is exchangeable with D_2O . Slow intermolecular exchange is observed in dimethyl sulfoxide as solvent so that the vicinal coupling in $H-Si-OH$ is detectable.



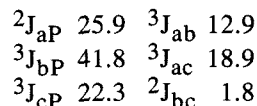
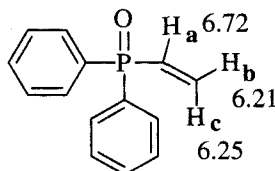
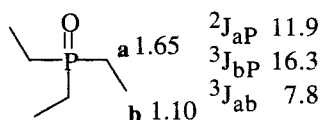
5.12.2

Phosphorus Compounds

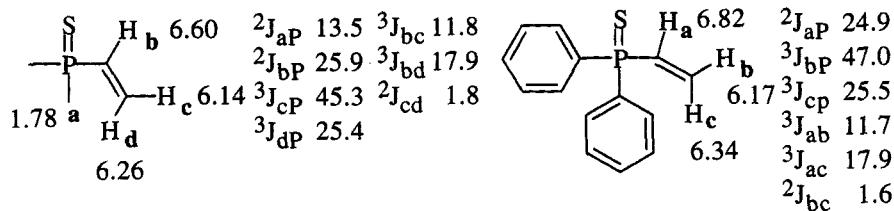
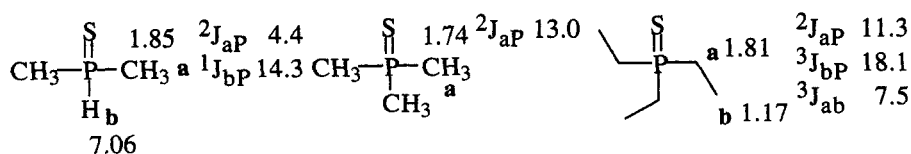
1H Chemical Shifts and Coupling Constants of Phosphines and Phosphonium Compounds (δ in ppm relative to TMS, $|J|$ in Hz)



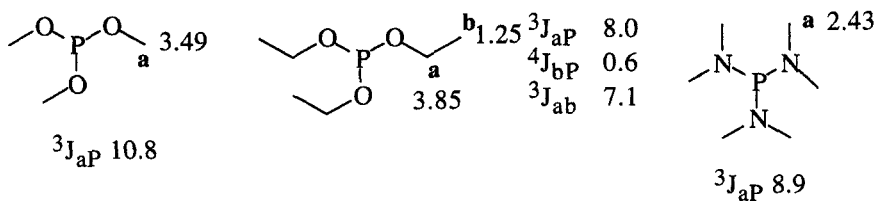
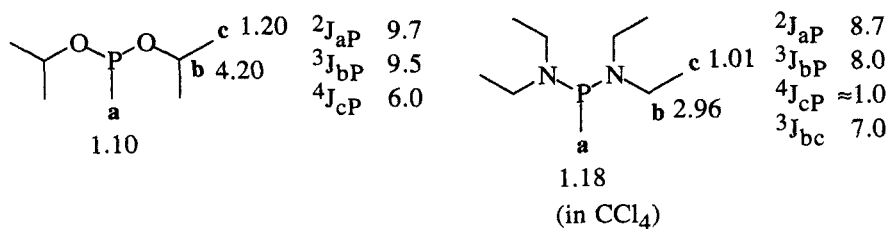
1H Chemical Shifts and Coupling Constants of Phosphine Oxides and Sulfides (δ in ppm relative to TMS, $|J|$ in Hz)



Misc.



^1H Chemical Shifts and Coupling Constants of Phosphonous Acid Derivatives (δ in ppm relative to TMS, $|J|$ in Hz)



¹H Chemical Shifts and Coupling Constants of Phosphonic and Phosphoric Acid Derivatives (δ in ppm relative to TMS, J in Hz)

<p> δ 3.66 (b), 1.43 (a) $2J_{aP}$ 17.3, $3J_{bP}$ 11.0 </p>	<p> δ 3.65 (c), 1.72 (a), 1.06 (b) $2J_{aP}$ -18.0, $3J_{bP}$ 19.5, $3J_{cP}$ 10.0, $3J_{ab}$ 7.5 </p>	<p> δ 7.40 (b), 7.72 (a), 7.48 (c, d, e) $3J_{aP}$ 13.3, $4J_{bP}$ 4.1, $5J_{cP}$ 1.2, $3J_{ab}$ 7.7, $4J_{ac}$ 1.4, $5J_{ad}$ 0.6, $4J_{ae}$ 1.6, $3J_{bc}$ 7.6, $4J_{bd}$ 1.4 </p>
<p> δ 3.78 (a), 1.29 (b) J_{aP} 11.0 </p>	<p> δ 4.04 (a), 1.29 (b) $3J_{aP}$ 8.5, $4J_{bP}$ 0.7, $3J_{ab}$ \approx 7 </p>	<p> δ 4.06 (a), 1.28 (b) $3J_{aP}$ 10.0, $4J_{bP}$ 0.7, $3J_{ab}$ \approx 7 </p>

¹H Chemical Shifts and Coupling Constants of Phosphorus Ylids (δ in ppm relative to TMS, J in Hz)

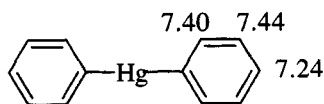
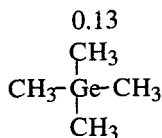
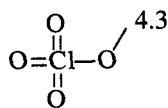
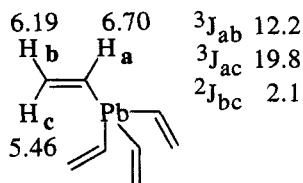
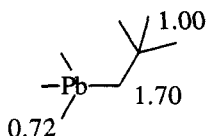
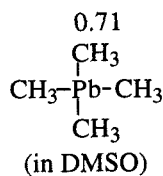
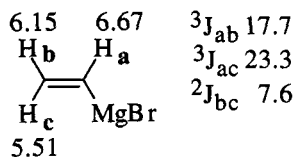
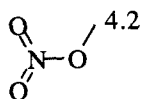
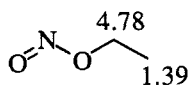
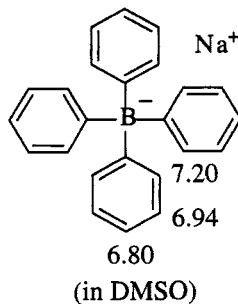
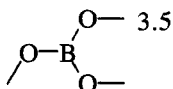
<p> δ 1.72 (a) $2J_{ab}$ 12.7, $2J_{ac}$ -1.2 </p>	<p> δ 1.82 (a) $3J_{ab}$ 15.9, $3J_{ac}$ 3.6 </p>
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5.12.3

Miscellaneous Compounds

^1H Chemical Shifts and Coupling Constants of Miscellaneous Compounds (δ in ppm relative to TMS)

$\text{Li}-\text{CH}_3$ -1.32 (in benzene)
-1.74 (in ether)

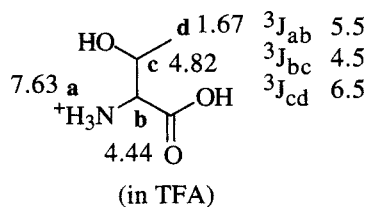
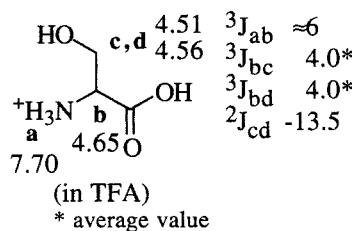
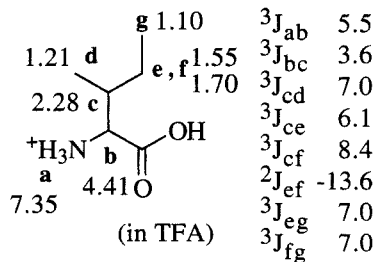
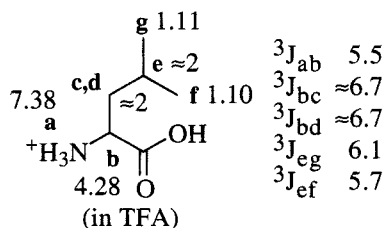
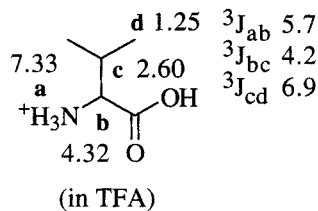
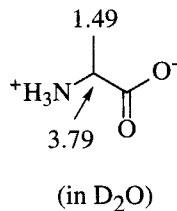
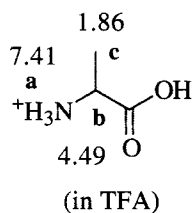
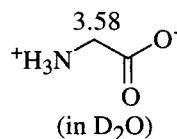
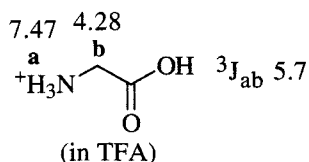


Misc.

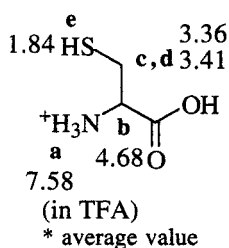
5.13 Natural Products

5.13.1 Amino Acids

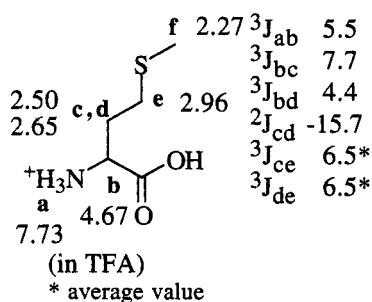
¹H Chemical Shifts and Coupling Constants of Amino Acids (δ in ppm relative to TMS; J in Hz, solvent: trifluoroacetic acid (TFA) or D₂O) [1]



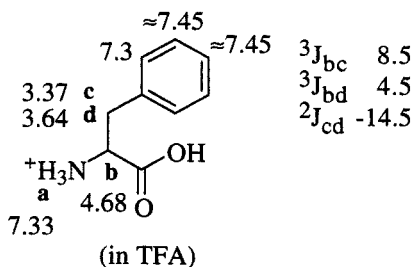
Natural
Products



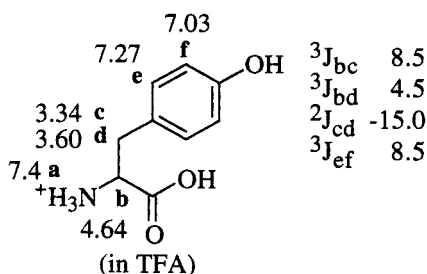
$^3J_{ab}$	5.3
$^3J_{bc}$	5.0*
$^3J_{bd}$	5.0*
$^2J_{cd}$	-15.5
$^3J_{ce}$	9.1*
$^3J_{de}$	9.1*



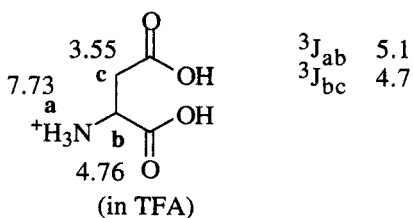
$^3J_{ab}$	5.5
$^3J_{bc}$	7.7
$^3J_{bd}$	4.4
$^2J_{cd}$	-15.7
$^3J_{ce}$	6.5*
$^3J_{de}$	6.5*



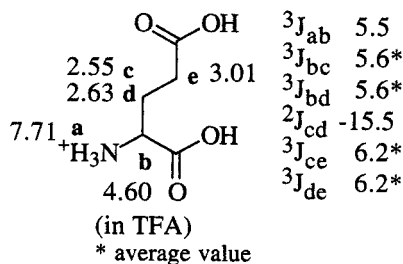
$^3J_{bc}$	8.5
$^3J_{bd}$	4.5
$^2J_{cd}$	-14.5



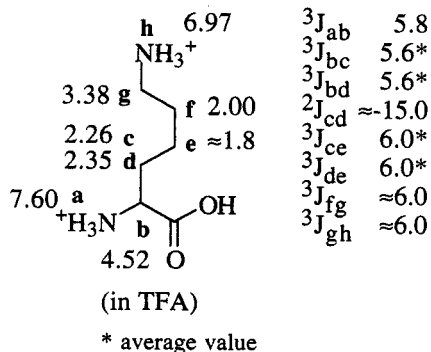
$^3J_{bc}$	8.5
$^3J_{bd}$	4.5
$^2J_{cd}$	-15.0
$^3J_{ef}$	8.5



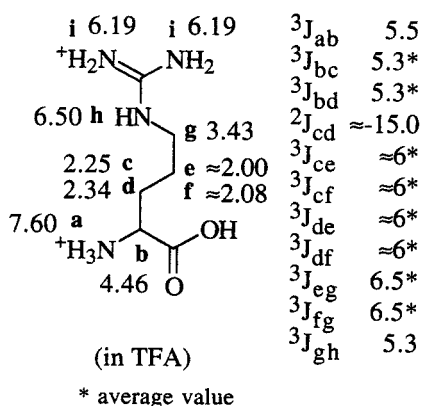
$^3J_{ab}$	5.1
$^3J_{bc}$	4.7



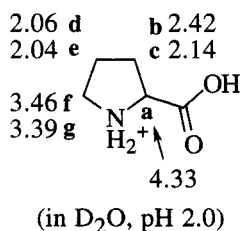
$^3J_{ab}$	5.5
$^3J_{bc}$	5.6*
$^3J_{bd}$	5.6*
$^2J_{cd}$	-15.5
$^3J_{ce}$	6.2*
$^3J_{de}$	6.2*



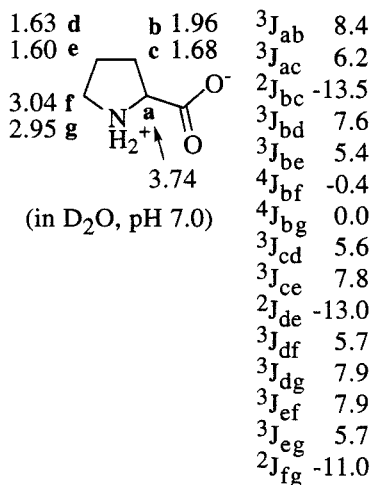
$^3J_{ab}$	5.8
$^3J_{bc}$	5.6*
$^3J_{bd}$	5.6*
$^2J_{cd}$	-15.0
$^3J_{ce}$	6.0*
$^3J_{de}$	6.0*
$^3J_{fg}$	6.0
$^3J_{gh}$	6.0



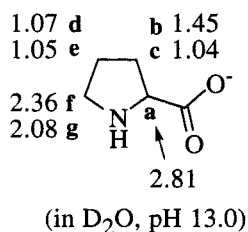
$^3J_{ab}$	5.5
$^3J_{bc}$	5.3*
$^3J_{bd}$	5.3*
$^2J_{cd}$	-15.0
$^3J_{ce}$	6.0*
$^3J_{cf}$	6.0*
$^3J_{de}$	6.0*
$^3J_{df}$	6.0*
$^3J_{eg}$	6.5*
$^3J_{fg}$	6.5*
$^3J_{gh}$	5.3



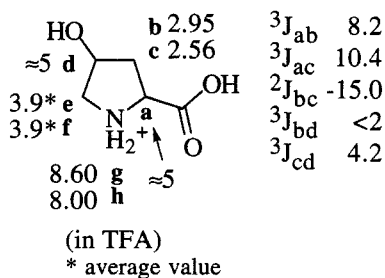
$^3J_{ab}$	8.5
$^3J_{ac}$	6.5
$^2J_{bc}$	-13.5
$^3J_{bd}$	7.5
$^3J_{be}$	5.5
$^4J_{bf}$	-0.4
$^4J_{bg}$	0.0
$^3J_{cd}$	5.5
$^3J_{ce}$	7.5
$^2J_{de}$	-13.0
$^3J_{df}$	5.5
$^3J_{dg}$	7.5
$^3J_{ef}$	7.5
$^3J_{eg}$	5.5
$^2J_{fg}$	-11.0



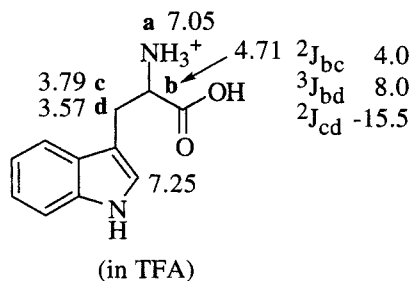
$^3J_{ab}$	8.4
$^3J_{ac}$	6.2
$^2J_{bc}$	-13.5
$^3J_{bd}$	7.6
$^3J_{be}$	5.4
$^4J_{bf}$	-0.4
$^4J_{bg}$	0.0
$^3J_{cd}$	5.6
$^3J_{ce}$	7.8
$^2J_{de}$	-13.0
$^3J_{df}$	5.7
$^3J_{dg}$	7.9
$^3J_{ef}$	7.9
$^3J_{eg}$	5.7
$^2J_{fg}$	-11.0



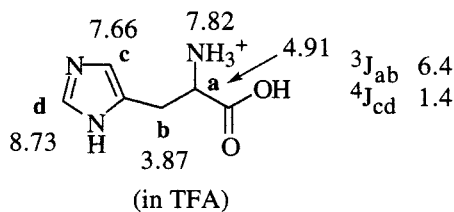
$^3J_{ab}$	8.6
$^3J_{ac}$	6.6
$^2J_{bc}$	-12.0
$^3J_{bd}$	8.1
$^3J_{be}$	5.9
$^4J_{bf}$	-0.6
$^4J_{bg}$	0.0
$^3J_{cd}$	6.7
$^3J_{ce}$	8.5
$^2J_{de}$	-11.0
$^3J_{df}$	5.5
$^3J_{dg}$	8.1
$^3J_{ef}$	7.7
$^3J_{eg}$	5.7
$^2J_{fg}$	-10.5



$^3J_{ab}$	8.2
$^3J_{ac}$	10.4
$^2J_{bc}$	-15.0
$^3J_{bd}$	<2
$^3J_{cd}$	4.2



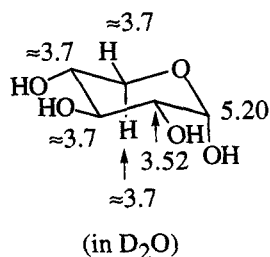
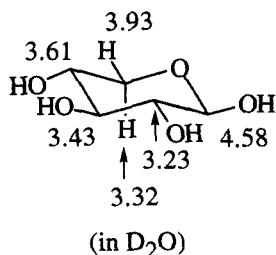
$^2J_{bc}$	4.0
$^3J_{bd}$	8.0
$^2J_{cd}$	-15.5



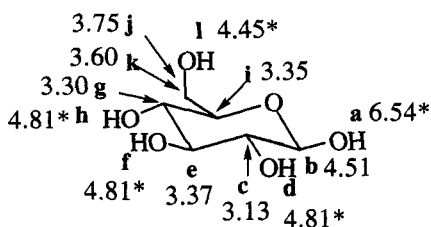
$^3J_{ab}$	6.4
$^4J_{cd}$	1.4

5.13.2

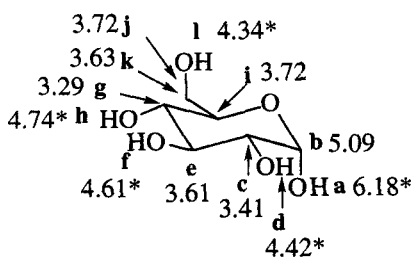
Carbohydrates [2-4]



Glucose

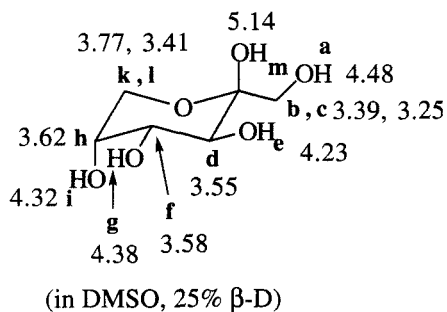


	In D_2O	In DMSO
$^3\text{J}_{bc}$	7.8	$^3\text{J}_{ab}$ 6.5
$^3\text{J}_{ce}$	9.5	$^3\text{J}_{cd}$ 4.5-6
$^3\text{J}_{eg}$	9.5	$^3\text{J}_{ef}$ 4.5-6
$^3\text{J}_{gi}$	9.5	$^3\text{J}_{gh}$ 4.5-6
$^3\text{J}_{ij}$	2.8	$^3\text{J}_{jl}$ 5.5
$^3\text{J}_{ik}$	5.7	$^3\text{J}_{kl}$ 6.0
$^2\text{J}_{jk}$	-12.8	

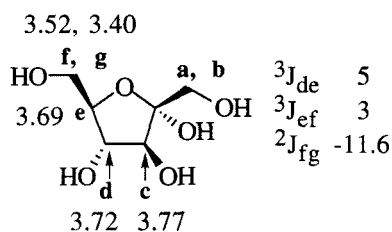


	In D_2O	In DMSO
$^3\text{J}_{bc}$	3.6	$^3\text{J}_{ab}$ 4.5
$^3\text{J}_{ce}$	9.5	$^3\text{J}_{cd}$ 6.8
$^3\text{J}_{eg}$	9.5	$^3\text{J}_{ef}$ 4.8
$^3\text{J}_{gi}$	9.5	$^3\text{J}_{gh}$ 5.5
$^3\text{J}_{ij}$	2.8	$^3\text{J}_{jl}$ 5.7
$^3\text{J}_{ik}$	5.7	$^3\text{J}_{kl}$ 6.2
$^2\text{J}_{jk}$	-12.8	

Fructose

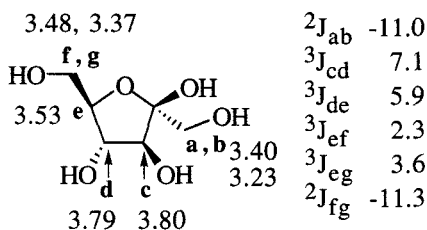


In DMSO (at 70 °C)	In DMSO (at 25 °C)	δ in D ₂ O (75% β -D)
$2J_{bc}$ -11.3	$3J_{ab}$ 7.4	b 3.68
$3J_{df}$ 10.1	$3J_{ac}$ 5.4	c 3.53
$3J_{fh}$ 4.0	$3J_{de}$ 6.8	d 3.76
$3J_{hk}$ 1.9	$3J_{fg}$ 5.8	f 3.86
$3J_{hl}$ 1.6	$3J_{hi}$ 3.8	h 3.96
$2J_{kl}$ -12.1		k 4.00
		l 3.68



Coupling constants: at 70 °C,
tentative values

$3J_{de}$	5
$3J_{ef}$	3
$2J_{fg}$	-11.6

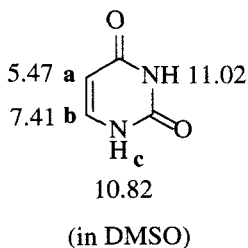
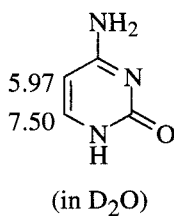


Coupling constants: at 70 °C

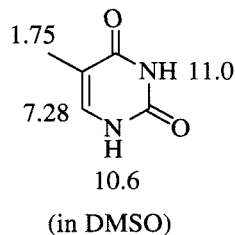
$2J_{ab}$	-11.0
$3J_{cd}$	7.1
$3J_{de}$	5.9
$3J_{ef}$	2.3
$3J_{eg}$	3.6
$2J_{fg}$	-11.3

5.13.3

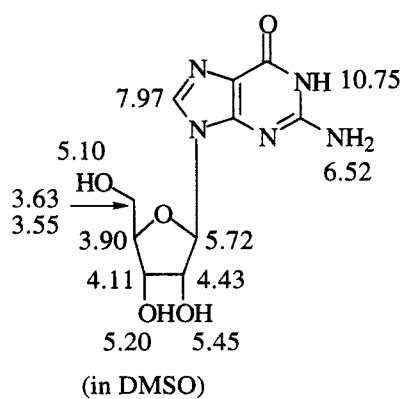
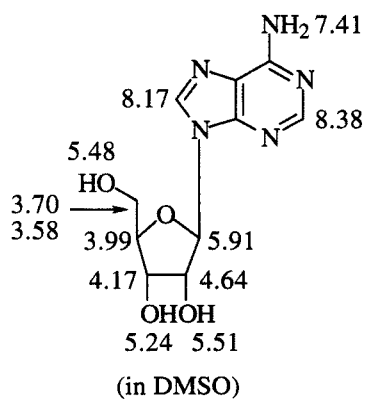
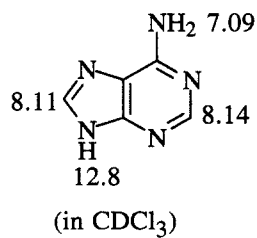
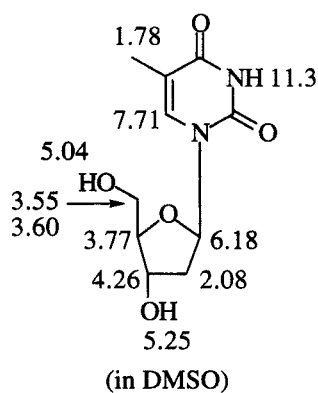
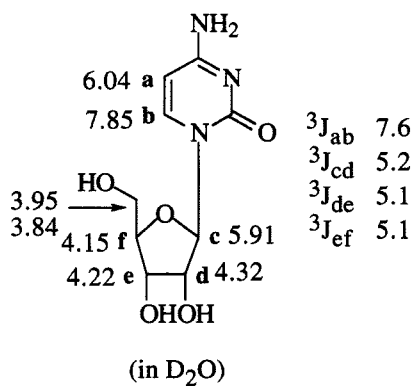
Nucleotides and Nucleosides

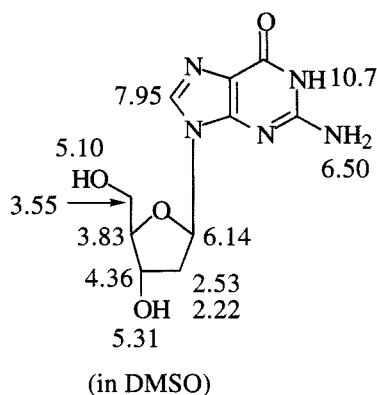
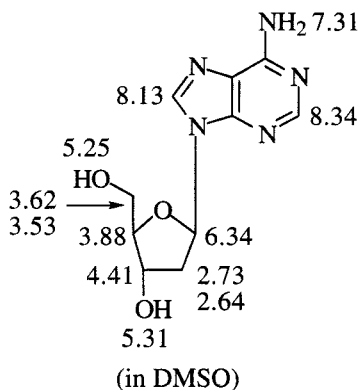


$3J_{ab}$	7.5
$3J_{bc}$	5.7



Natural
Products





5.13.4

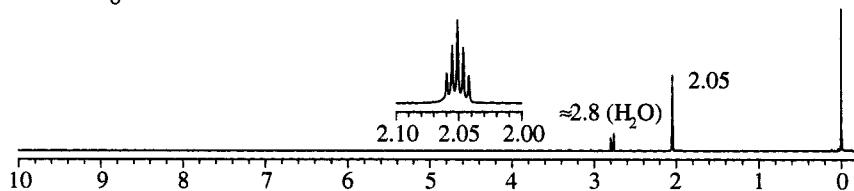
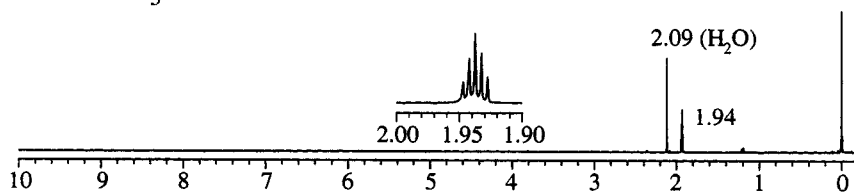
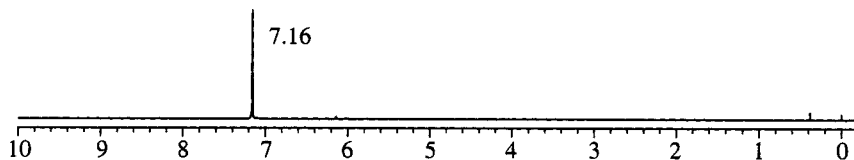
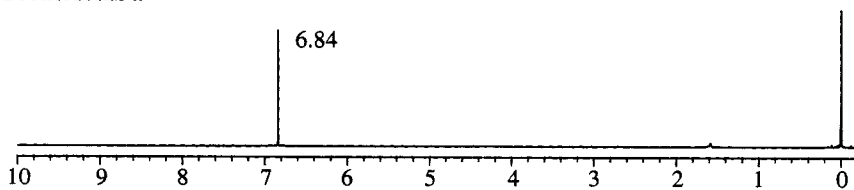
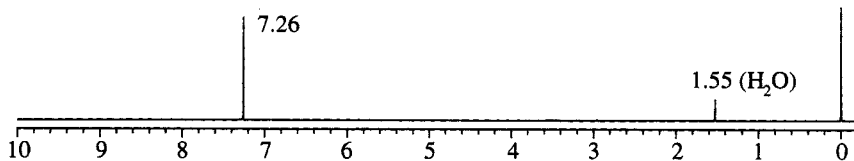
References

- [1] B. Bak, C. Dambmann, F. Nicolaisen, E.J. Pedersen, N.S. Bhacca, Proton magnetic resonance at 220 MHz of amino acids, *J. Mol. Spectrosc.* **1968**, 26, 78.
- [2] B. Gillet, D. Nicole, J.-J. Delpuech, B. Gross, High field nuclear magnetic resonance spectra of hydroxyl protons of aldoses and ketoses, *Org. Magn. Reson.* **1981**, 17, 28.
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- [4] C. Altona, C.A.G. Haasnoot, Prediction of *anti* and *gauche* vicinal proton-proton coupling constants in carbohydrates: a simple additivity rule for pyranose rings, *Org. Magn. Reson.* **1980**, 13, 417.

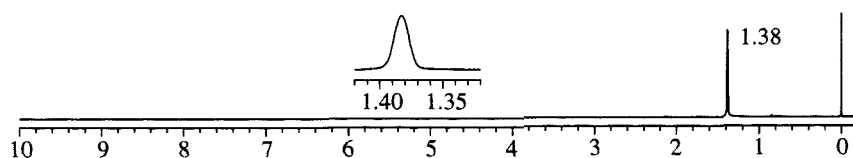
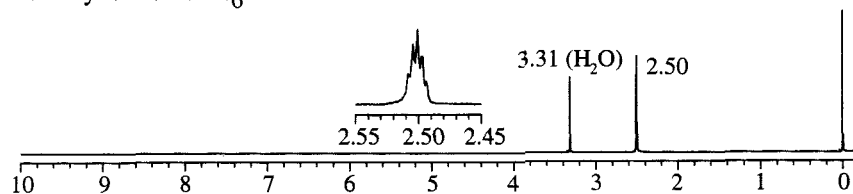
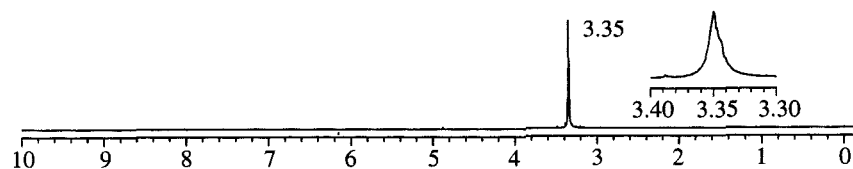
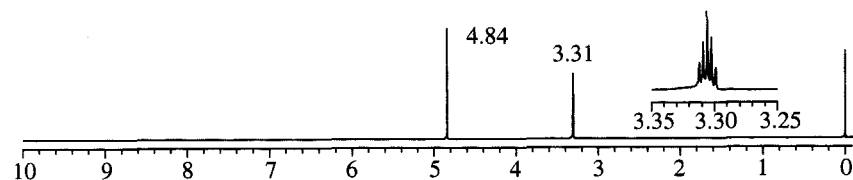
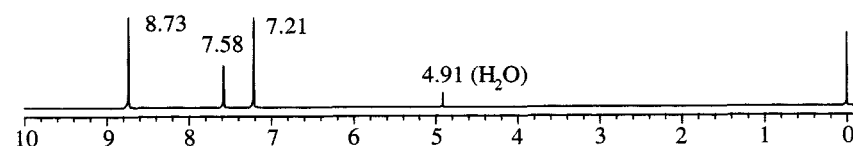
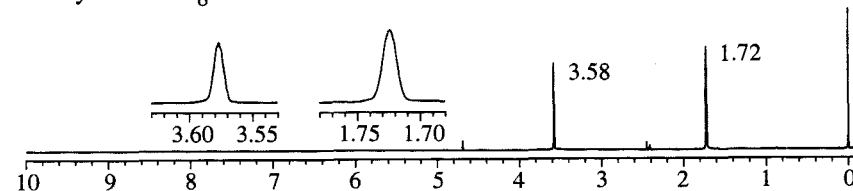
5.14

Spectra of Solvents and Reference Compounds

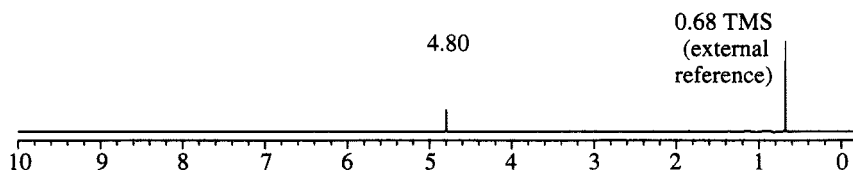
5.14.1

 ^1H NMR Spectra of Common Deuterated Solvents(500 MHz; $\approx 1'000$ data points per 1 ppm; δ in ppm relative to TMS)Acetone- d_6 Acetonitrile- d_3 Benzene- d_6 Bromoform- d Chloroform- d 

Solvents

Cyclohexane- d_{12} Dimethyl sulfoxide- d_6 Methanol- d_1 Methanol- d_4 Pyridine- d_5 Tetrahydrofuran- d_8 

Solvents

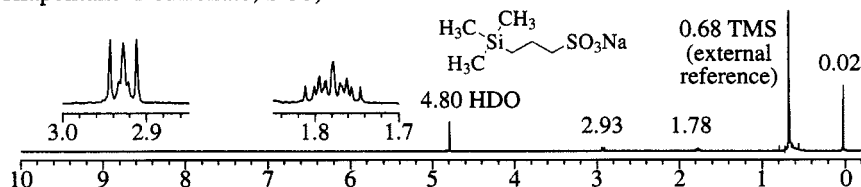
Water- d_2 

5.14.2

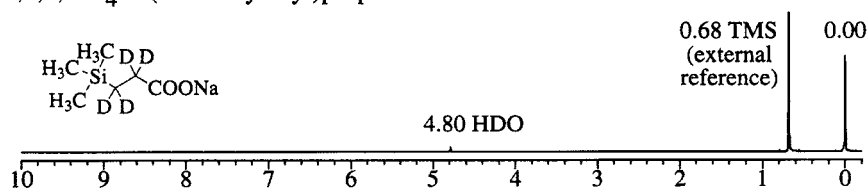
 ^1H NMR Spectra of Secondary Reference Compounds

Chemical shifts in ^1H NMR spectra are usually reported relative to the peak position of tetramethylsilane (TMS) added to the sample as an internal reference. If TMS is not sufficiently soluble, a capillary with TMS may be used as external reference. In this case, owing to the different volume susceptibilities, the local magnetic fields in solvent and reference differ, and the peak position of the reference must be corrected. For a D_2O solution in a cylindrical sample and neat TMS in a capillary, the correction amounts to +0.68 and -0.34 ppm for superconducting and electromagnets, respectively. These values must be subtracted from the chemical shifts relative to external TMS if its position is set to 0.00 ppm. Alternatively, secondary references with $(\text{CH}_3)_3\text{SiCH}_2$ groups may be used. The following spectra of two such secondary reference compounds in D_2O were measured at 500 MHz with TMS as external reference. Chemical shifts are reported in ppm relative to TMS upon correction for the difference in the volume susceptibilities of D_2O and TMS. As a result, the peak for the external TMS appears at 0.68 ppm.

3-(Trimethylsilyl)-1-propanesulfonic acid sodium salt (sodium 4,4-dimethyl-4-silapentane-1-sulfonate; DSS)



2,2,3,3- D_4 -3-(Trimethylsilyl)propionic acid sodium salt

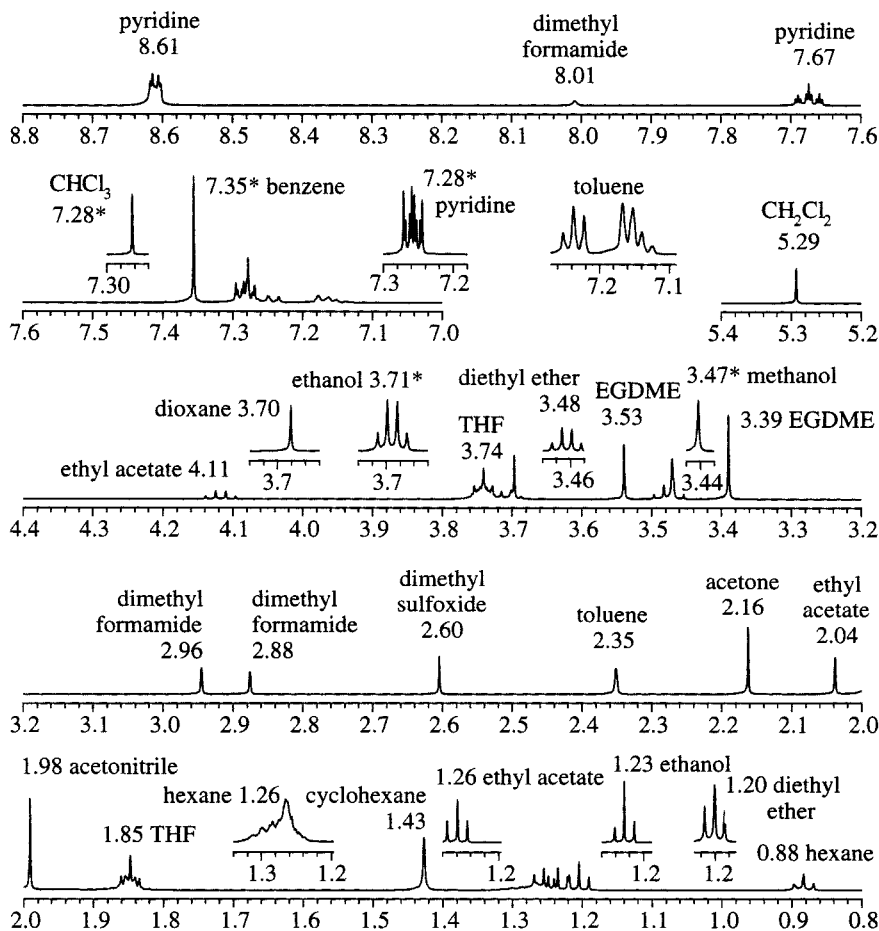


Solvents

5.14.3

 ^1H NMR Spectrum of a Mixture of Common Nondeuterated Solvents

The following ^1H NMR spectrum (500 MHz, δ in ppm relative to TMS) of CDCl_3 containing 18 common solvents (0.05–0.4 vol%) is shown as a guide for the identification of possible impurities. Where the signals of several solvents overlap, insets show signals for the individual compounds from separate spectra. Peaks in these insets are labeled with the corresponding chemical shifts from the main spectrum but their values may differ by up to 0.03 ppm. Signals that are particularly prone to vary in their position are marked with *. THF: tetrahydrofuran; EGDME: ethylene glycol dimethyl ether.

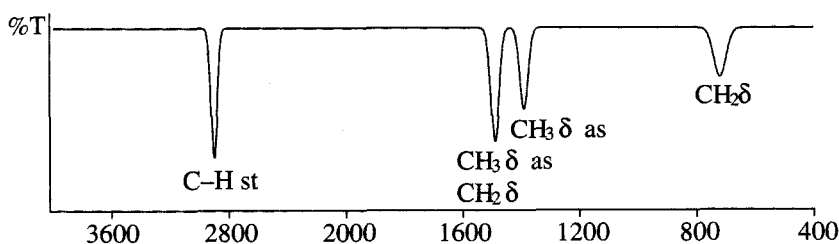


Solvents





6 IR Spectroscopy



6.1 Alkanes



Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
C-H st	3000–2840	Intensity variable, often multiplet
	<i>Beyond normal range:</i>	
	2850–2815	CH ₃ –O, methyl ethers
	2880–2830	CH ₂ –O, ethers
	2880–2835, 2780–2750	O–CH ₂ –O, methylenedioxy
	≈2820	O–CH–O, acetals: weak
	3050–3000	 O,  N
	2900–2800, 2780–2750	CH=O, aldehydes: Fermi resonance
	2820–2780	CH ₃ –N, CH ₂ –N; amines
	3100–3050, 3035–2995	
	≈2700	 comb for cyclohexanes (CH ₂ as st ≈2930)
	3080–2900	CH–hal



Assignment	Range	Comments
CH₃ δ as	1470–1430	Medium, coincides with CH ₂ δ
	<i>Beyond normal range:</i>	
	1440–1400	CH ₃ –C=O, methyl ketones, acetals CH ₃ –C=C
CH₂ δ	1475–1450	Medium, coincides with CH ₃ δ as
	<i>Beyond normal range:</i>	
	≈1440	CH ₂ –C=C CH ₂ –C≡C
	≈1425	CH ₂ –C=O, CH ₂ –C≡N, CH ₂ –X (X: hal, NO ₂ , S, P)
CH₃ δ sy	1395–1365	Medium. Doublet in compounds with geminal methyl groups:
	≈1385, ≈1370	CH(CH ₃) ₂ , equal intensity (γ: 1175–1140, d)
	≈1385,	C(CH ₃) ₂ , 1385 weaker than 1365
	≈1365	(γ: 1220–1190, often d)
	≈1390,	C(CH ₃) ₃ , of equal intensity, sometimes triplet
	≈1365	(γ: 1250–1200, d) N(CH ₃) ₂ , no doublet
		Solid-state spectra: sometimes doublet also in the absence of geminal methyl groups
	<i>Beyond normal range:</i>	
	1325–1310	SO ₂ –CH ₃
	1330–1290	S–CH ₃ , sulfides
	1310–1280	P–CH ₃
	1275–1260	Si–CH ₃ , strong, sharp
CH₃ γ	1250–800	Intensity variable, of no practical significance Strong band in compounds with geminal methyl groups:
	1175–1140	CH(CH ₃) ₂ , doublet
	1220–1190	C(CH ₃) ₂ , generally doublet
	1250–1200	C(CH ₃) ₃ , doublet, often not resolved
	<i>Beyond normal range:</i>	
	≈765	SiCH ₃
	≈855, ≈800	Si(CH ₃) ₂
	≈840, ≈765	Si(CH ₃) ₃

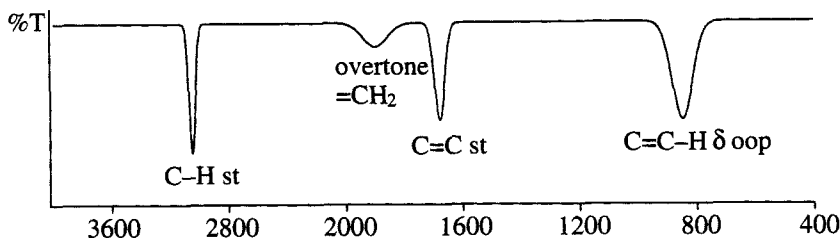
Assignment	Range	Comments
CH₂ γ	770–720	Medium, sometimes doublet C–(CH ₂) _n –C for n > 4 at \approx 720; for n < 4 at higher wavenumbers; in cyclohexanes at \approx 890, weaker
	<i>Beyond normal range:</i> 1060–800	Cycloalkanes, numerous bands, unreliable
C–D σ	2200–2080	In general, substitution of L by isotope L': $\nu_{X-L'} = \nu_{X-L} \sqrt{\frac{1/m_X + 1/m_{L'}}{1/m_X + 1/m_L}}$



6.2 Alkenes










6.2.1 Monoenes






Typical Ranges (ν in cm^{-1})




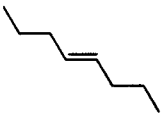
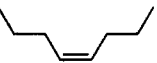

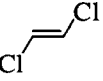

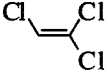

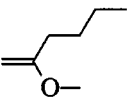
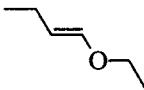
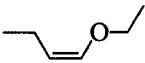
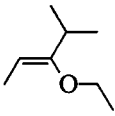
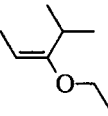
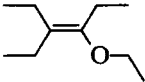
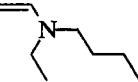
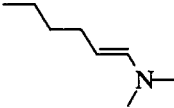
Assignment	Range	Comments
$=\text{CH}_2$ st	3095–3075	Medium, often multiple bands
$=\text{CH}$ st	3040–3010	Medium, often multiple bands CH st in aromatics and three-membered rings fall in the same range
<i>In cyclic compounds:</i>		
≈ 3075		
≈ 3060		
≈ 3045		
≈ 3020		
$=\text{CH}$ δ ip	1420–1290	Of no practical significance
$=\text{CH}$ δ oop	1005–675	A number of bands <i>In the same range also:</i> ar CH δ oop, C–O–C γ , and C–N–C γ in saturated heterocyclics, OH δ oop in carboxylic acids, NH γ , NO st, SO st, CH ₂ γ , CF st, CCl st


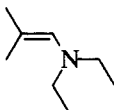


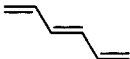

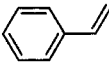

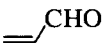



Assignment	Range	Comments
<i>Subranges:</i>		
	C=C	C=C-C=O C=C-OR C=C-O-C=O
CH=CH ₂	1005–985 920–900 (with overtone ≈810 at 1850–1800)	≈980 ≈960 ≈960 ≈815 ≈950 ≈870
		C = C
C=CH ₂	900–880 (with overtone ≈810 at 1850–1780)	≈940 ≈795
	990–960	≈975 ≈960 ≈950
	725–675	≈820
	840–800	≈820
C=C st	1690–1635	Of variable intensity, weak for highly symmetric compounds, strong for N=C=C and O=C=C
	<i>Subranges:</i>	
	1650–1635	CH=CH ₂
	1660–1640	C=CH ₂
	1690–1665	 Weak
	1665–1635	
	1690–1660	 Weak, often absent
	1690–1650	 Weak, often absent
	<i>Beyond normal range:</i>	
	down to ≈1590	C=C-X with X: O, N, S; of higher intensity; in vinyl ethers often doublet due to rotational isomers

At lower frequency if conjugated with:

C=C	C=C	≈1650 ≈1600		≈1630
	C≡C	≈1600		≈1640
	C≡N	≈1620		≈1640
	C=O	≈1630		

Examples (ν in cm^{-1})


	1645 994 912		1647 889 669		1682 972 963
	1670 968		1650 709		1667 825
	1575 826 761		1595 848 714		1587 929 835 780
	liquid: CCl ₄ : 1610 1634 1608 987 964 810 943		1655 1592 958 793		1670 1652 937 925
	1663		1660		1673
	1663		1628		1650

	1640		1662		
	1652 1612		1830 1621 987 818		1800 1621 941 899
	1607 (2270)		1636		1645 1612
	1618 (1704)		1618 (1684)		1635 1615 (1730) (1706)
	1637 (1735)				

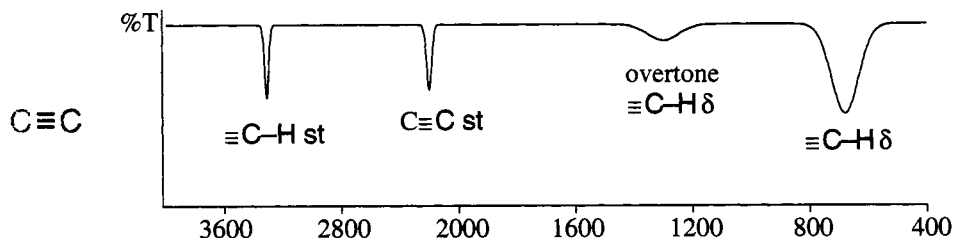
C=C

C=C

6.2.2 Allenenes

Assignment	Range	Comments
$(C=C)=C-H$ st	3050–2950	
$C=C=C$ st as	1950–1930	Strong, doublet in $X-C=C=CH_2$ if X other than alkyl Ring strain increases frequency:  ≈ 2020
$C=C=C$ st sy	1075–1060	Weak, absent with highly symmetric substitution
$(C=C)=CH_2$ δ oop	≈ 850	Strong, overtone at ≈ 1700 , weak

6.3 Alkynes

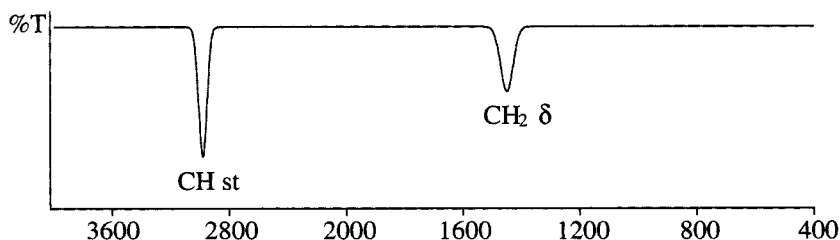


Typical Ranges (ν in cm^{-1})

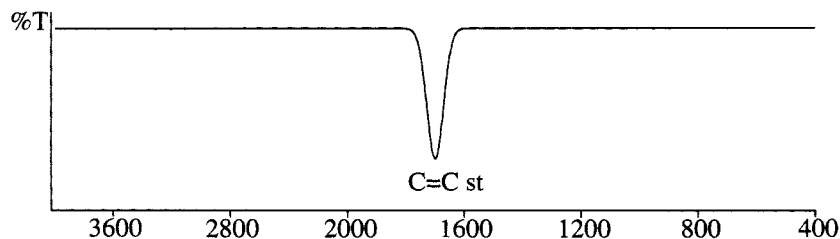
Assignment	Range	Comments
$\equiv\text{C-H}$ st	3340–3250	Strong, sharp; in the same region also OH st, NH st
$\text{C}\equiv\text{C}$ st	2260–2100	Weak, sharp
<i>Beyond normal range:</i>		
		R–C \equiv C–H; at the lower end of the cited range
		R–C \equiv C–R; usually 2 bands (Fermi resonance), often missing if symmetrical
<i>Subranges:</i>		
	≈ 2120	C–C \equiv C–H
	≈ 2220	C–C \equiv C–C
	≈ 2240	C–C \equiv C–CN
	≈ 2240	C–C \equiv C–COOH
	$\approx 2240, \approx 2140$	C–C \equiv C–COOCH ₃
<i>In the same range: C\equivZ st, X=Y=Z st, Si–H st</i>		
$\equiv\text{C-H}$ δ	700–600	Strong, broad; overtone at 1370–1220 (broad, weak)

6.4 Alicyclics

Cyclic Alkanes



Cyclic Alkenes

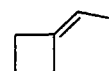
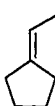
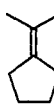
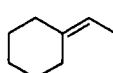
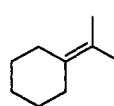


The other vibrations are similar to those in noncyclic alkenes and cyclic alkanes.

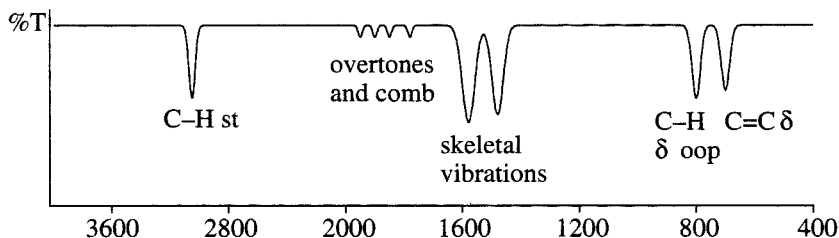
Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
C-H st	3090–2860	Strong
H-C-H δ	1470–1430	Weak
C=C st	1780–1610	Varies with ring size and substitution


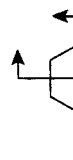
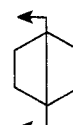

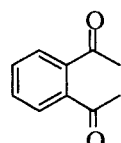
Twisting and wagging CH_2 as well as C-C st do not significantly differ from the corresponding vibrations in noncyclic compounds and are of limited diagnostic value.

Examples (ν in cm^{-1})3090
3019
2933
14342974
2896
14502951
2871
14552920
2860
14472933
2865
14622941
1471
1451 ≈ 1640  ≈ 1780  ≈ 1650  ≈ 1570  ≈ 1640  ≈ 1680  ≈ 1690  ≈ 1610  ≈ 1660  ≈ 1660  ≈ 1670  ≈ 1690  ≈ 1570  ≈ 1650  ≈ 1675  ≈ 1650  ≈ 1665  ≈ 1670  ≈ 1615

6.5 Aromatic Hydrocarbons



Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
arC-H st	3080–3030	Often numerous bands; in the same range also CH st of alkenes and small rings
arC-C	1625–1575	  <p>Medium, often doublet; generally weak in benzene derivatives having a center of symmetry in the ring</p> <p><i>In the same range also:</i> C=C st, C=N st, C=O st, N=O st, C-C in heterocyclics, NH δ</p>
	1525–1475	<p>Medium, often doublet:</p>   <p>Weak in:</p>  <p><i>In the same range:</i> C=O st, N=O st, C-C in heterocyclics, B-N st, CH₃ δ, CH₂ δ, NH δ</p>
comb	2000–1650	<p>Very weak; useful for determining substitution patterns in 6-membered aromatic rings</p> <p><i>In the same range also:</i> C=O st, B-H\cdotsB st, N⁺-H st, H₂O δ</p>



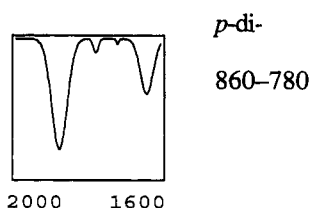
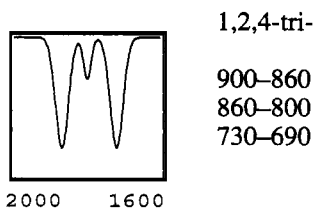
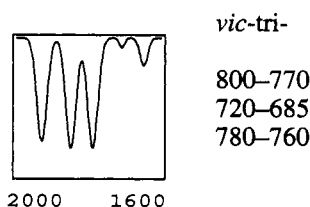
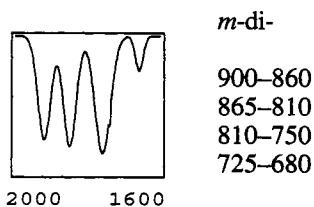
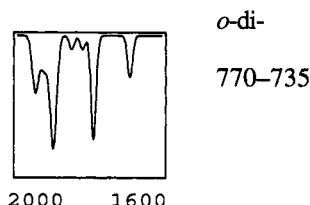
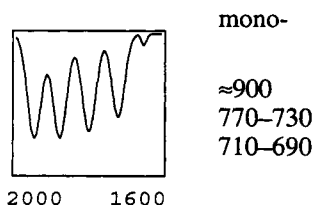
Assignment	Range	Comments
arC-H δ ip	1250-950	Numerous bands of variable intensity; of no practical significance
arC-H δ oop	900-650	One or more strong bands; useful for determining substitution patterns in 6-membered aromatic rings
<i>In the same range also: =C-H δ oop, C-O-C γ and C-N-C γ in saturated heterocyclics, OH δ oop in carboxylic acids, NH δ, N-O st, S-O st, CH₂ γ, C-F δ, C-Cl st</i>		

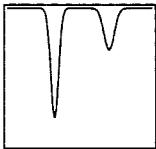
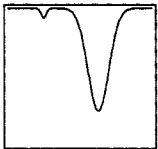
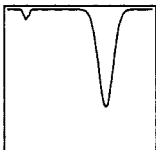
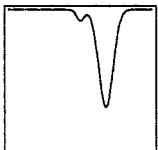
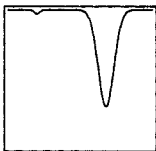
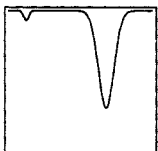


Determination of Substitution Patterns in 6-Membered Aromatic Rings: Position and Shape of Bands Related to the Number of Adjacent H-Atoms (ν in cm^{-1})

Not to be used for ring systems with strongly conjugated substituents such as C=O, NO₂, C \equiv N.

Comb, overtones	Substitution type; CH δ oop, ar C-C γ	Comb, overtones	Substitution type; CH δ oop, ar C-C γ
-----------------	--	-----------------	--



Comb, overtones	Substitution type; CH δ oop, ar C-C γ	Comb, overtones	Substitution type; CH δ oop, ar C-C γ
	1,2,3,4-tetra- 860–780		1,3,5-tri- 900–840 850–800 730–675
	1,2,3,5-tetra- 900–840		1,2,4,5-tetra- 900–840
	penta- 900–840		hexa- —



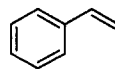
Examples (ν in cm^{-1})



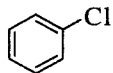
3080
3040
1968
1818



3021
1945
1862
1808
1739



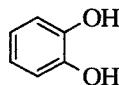
3086



3080



3040
1915
1845
1775

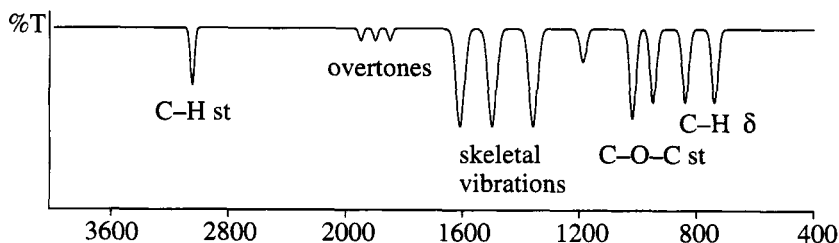


1927
1887
1764

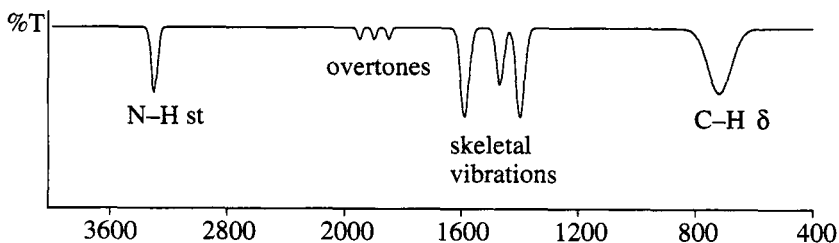
6.6 Heteroaromatic Compounds

Characteristic Absorption Bands (ν in cm^{-1})

Furans






Pyrroles



Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
N-H st	3450–3200	Medium, narrow; shifted by formation of hydrogen bonds
Overtones	2100–1800	Weak, characteristic
Ring skeleton	1610–1360	Strong, sharp bands
C-H δ	1000–700	Strong, broad; difficult to identify
C-H st	3100–3000	Medium, sharp
CO-C st	1190–990	Medium or strong; of variable intensity

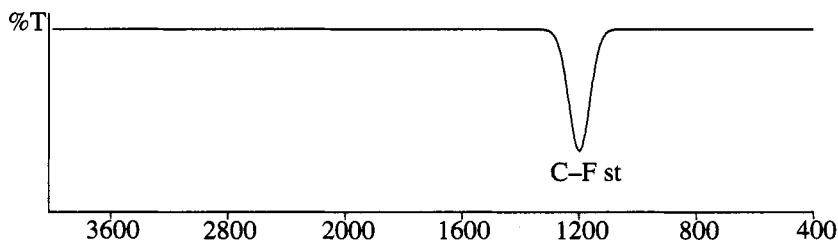
5-Ring-Heteroaromatics:

			
NH st free		3500–3400	
NH st H-bonded		3400–2800	
CH st	≈3100	≈3100	≈3100
Ring skeleton: intensity	1610–1560	1590–1560	1535–1515
variable, generally multiplets	1510–1475	1540–1500	1455–1410
CH δ oop: generally strong	990–725	770–710	935–700



6.7 Halogen Compounds

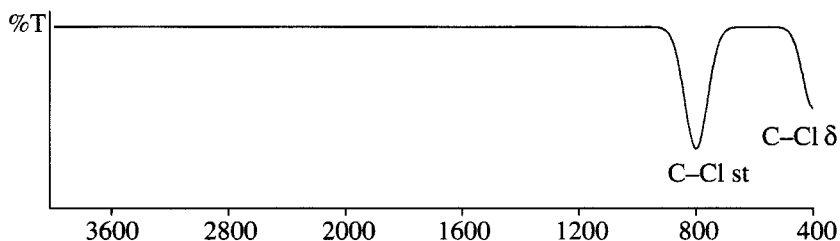
6.7.1 Fluoro Compounds



Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
Hal C-F st	1400–1000	Strong, often more than one band (rotational isomers), often not resolved
	<i>Subranges:</i>	
	1100–1000	al CF_2 (FC-H st: 3080–2990)
	1150–1000	al CF_2
	1350–1100	al CF_3
	1350–1150	C=CF
	≈ 1745	C=CF ₂ st
	1250–1100	ar CF
	<i>In the same range:</i> strong bands for C–O st, NO ₂ st sym, C=S st, S=O st	
CF ₂	780–680	Medium or weak, assignment uncertain
CF ₃	780–680	(C–F δ ?)
S–F st	815–755	Strong
P–F st	1110–760	
Si–F st	980–820	
B–F st	1500–800	

6.7.2 Chloro Compounds

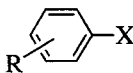


Typical Ranges (ν in cm^{-1})

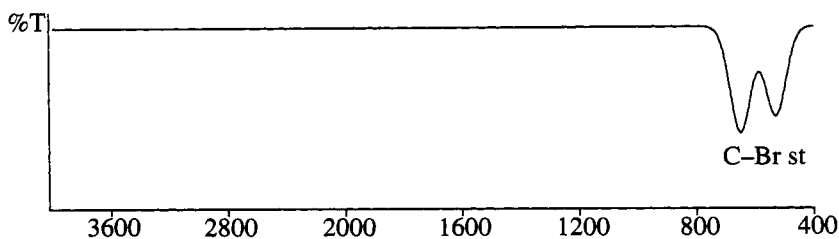
Assignment	Range	Comments
C-Cl st	1100–1020	Strong, narrow or of medium width; chloroaromatics
	830– <600	Strong, often broad (rotational isomers), absent in chloroaromatics
C-Cl δ	400–280	Of medium strength and width
P-Cl st	<600	
Si-Cl st	<625	
B-Cl st	1100–650	

Hal

In disubstituted halobenzenes, characteristic skeletal vibrations:

	X	<i>ortho</i>	<i>meta</i>	<i>para</i>
	Cl	1055–1035	1080–1075	1095–1090
	Br	1045–1030	1075–1065	1075–1070
	I			1060–1055

6.7.3 Bromo Compounds

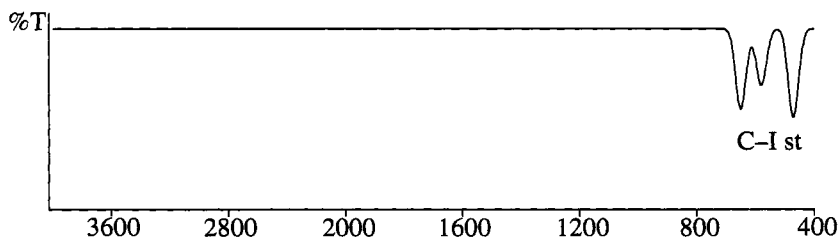


Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
C-Br st	1080–1000	Strong, narrow or of medium width; bromoaromatics
	700–500	Strong, of medium width; absent in bromoaromatics
C-Br δ	350–250	Of medium strength and width

Hal

6.7.4 Iodo Compounds



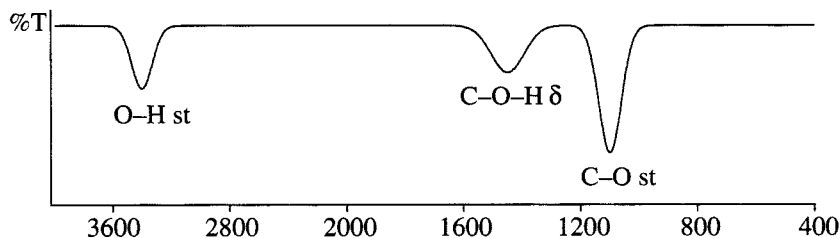
Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
C-I st	650–450	Strong, two or more bands
C-I δ	300–50	Of medium strength and width

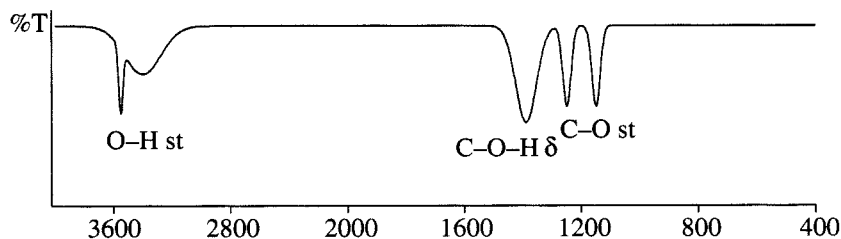
6.8 Alcohols, Ethers, and Related Compounds

6.8.1 Alcohols and Phenols

Alcohols



Phenols

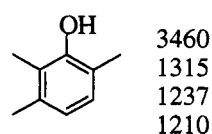
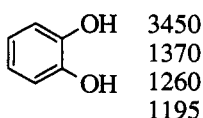
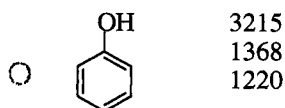
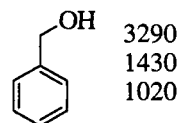
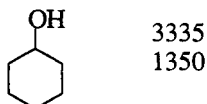
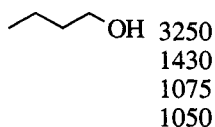


Typical Ranges (ν in cm^{-1})

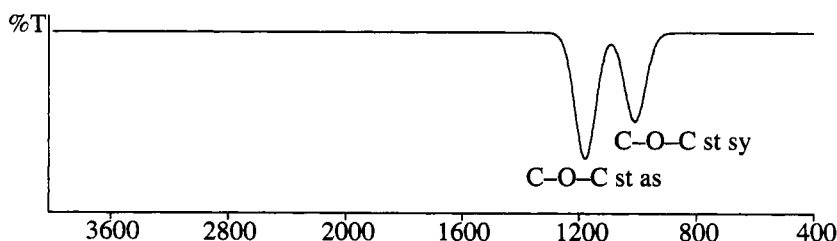
Assignment	Range	Comments
O-H st	3650–3200	Of variable intensity
	<i>Subranges:</i>	
	3650–3590	Free OH; sharp
	3550–3450	Hydrogen bonded OH; broad
	3500–3200	Polymer OH; broad, often numerous bands
	<i>Beyond normal range:</i>	
	3200–2500	Enols, chelates; often very broad
	<i>In the same range also:</i> NH st, $\equiv\text{CH}$ st (≈ 3300 , sharp), H_2O	
O-H δ ip	1450–1200	Medium, of no practical significance

Assignment	Range	Comments
C-O st	1260–970	Strong, often doublet
	<i>Subranges:</i>	
	1075–1000	CH ₂ -OH
	1125–1000	CH-OH
	1210–1100	C-OH
	1275–1150	ar C-OH
	<i>In the same range:</i> bands for C-F st, C-N st, N-O st, P-O st, C=S st, S=O st, P=O st, Si-O st, Si-H δ	
O-H δ oop	<700	Medium, of no practical significance

Examples (ν in cm^{-1})



6.8.2 Ethers, Acetals, Ketals






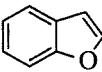


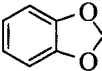


In acetals and ketals, the C-O stretching vibrations are split into 3, sometimes even 4 to 5 bands.

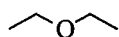
Acetals have an additional band due to a special C-H δ vibration.

The C-H st vibration frequency is especially low: OCH₃ st, 2850–2815;

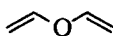
OCH₂ st, 2880–2835.

Typical Ranges (ν in cm^{-1})

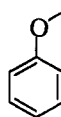
Assignment	Range	Comments
C–O–C st as	1310–1000	Strong, sometimes split
	<i>Subranges for non-cyclic ethers:</i>	
	1150–1085	$\text{CH}_2\text{--O--CH}_2$
	1170–1115	CH--O--CH , often split
	1225–1180	C=C--O--alC
	1275–1200	arC--O--alC
	<i>Subranges for cyclic ethers:</i>	
	1280 sym	
	870 as	
	≈ 1030 sym	
	≈ 980 as	
	≈ 1070 sym	
	≈ 915 as	
	≈ 1235	
	≈ 1100 as	
	≈ 815 sym	
	≈ 950	 ketals, acetals: 4 to 5 bands
	≈ 925	
	1024, 1086 as ≈ 880 sym	
	≈ 800	 in acetals: st CH, ≈ 2820 , weak
C–O–C st sym	1055–870	Strong, sometimes multiple bands
	<i>Subranges for non-cyclic ethers:</i>	
	1125–1080	C=C--O--alC , medium
	1075–1020	arC--O--alC , medium
	<i>In the same range: strong bands for C–O st, C–F st, C–N st, N–O st, P–O st, C=S st, S=O st, P=O st, Si–O st, Si–H δ</i>	

Examples (ν in cm^{-1})

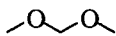
1136
935
917



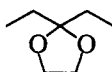
1225
1218
1211
1003



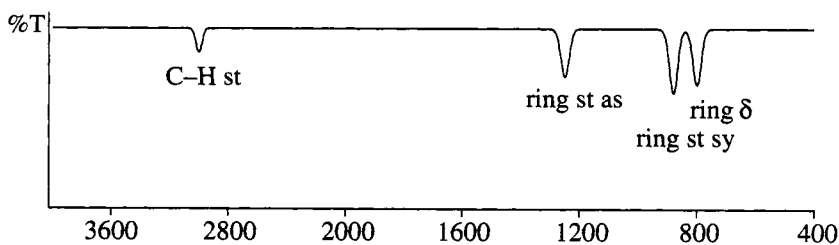
1250
1040



1188
1138
1111
1046



1172
1132
1077
1057
1038

6.8.3 Epoxides**Typical Ranges** (ν in cm^{-1})

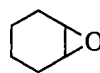
Assignment	Range	Comments
C-H st	3050–2990	Frequency higher than normally found in alkanes
ring st as	1280–1230	Variable intensity
ring st sy	950–815	Variable intensity
ring def	880–750	Variable intensity

Examples (ν in cm^{-1})

1280
870

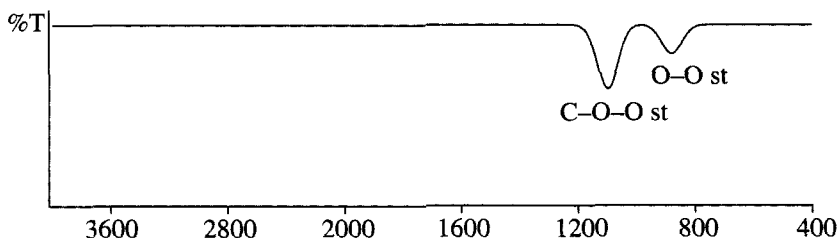


1230 sy
885 as
845 δ



1260 sy
890 as
780 δ

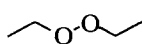
6.8.4 Peroxides and Hydroperoxides



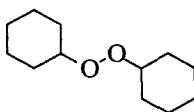
Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
O-O-H st	3450–3200	Of variable intensity
	<i>Subranges:</i>	
	≈ 3450	Free OOH; H-bonded: $\approx 30 \text{ cm}^{-1}$ higher than in corresponding alcohols
		<i>In the same range:</i> OH st, NH st, $\equiv\text{CH}$ st, H_2O
C-O-O st	1200–1000	Strong, about $\approx 20 \text{ cm}^{-1}$ lower than in corresponding alcohols
		<i>In the same range:</i> strong bands for C-O st, C-F st, C-N st, N-O st, P-O st, C=S st, S=O st, P=O st, Si-O st, Si-H δ
O-O st	1000–800	Medium or weak, often doublet, assignment uncertain
Also:	1760–1745	C=O st in peracids
	1820–1770	C=O st in diacylperoxides (two bands)

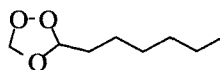
Examples (ν in cm^{-1})



1017
880



1070
1060
943

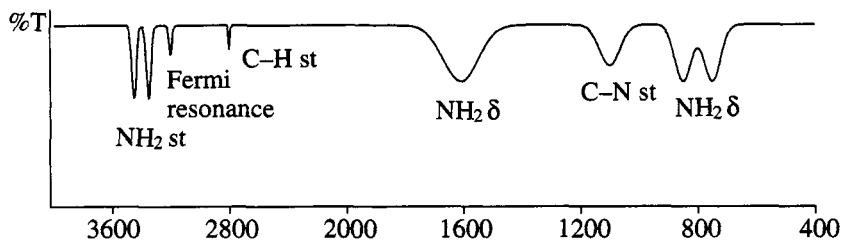


1100
852

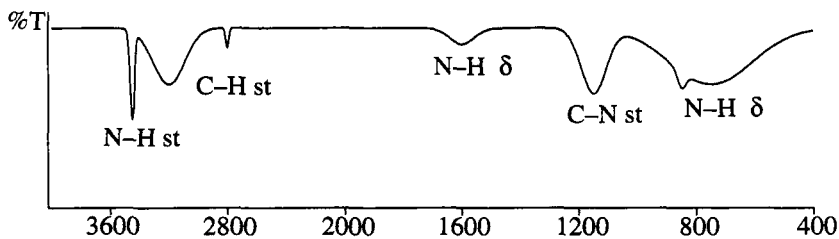
6.9 Nitrogen Compounds

6.9.1 Amines and Related Compounds

Primary Amines

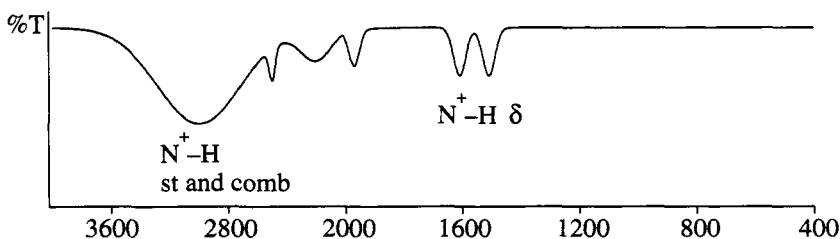


Secondary Amines



N

Ammonium



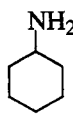
Typical Ranges (ν in cm^{-1})

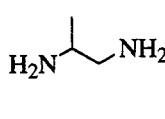
Assignment	Range	Comments
NH_2 st	3500–3300	Of variable intensity, generally 2 sharp bands, $\Delta\nu = 65\text{--}75$ At lower wavenumbers (<3200) and broader if H-bonded. Free and H-bonded forms often simultaneously observed In primary aromatic amines additional combination band at ≈ 3200 <i>In the same range:</i> OH st, $\equiv\text{CH}$ st
NH st	3450–3300	Of variable intensity, only one band At lower wavenumbers (<3200) and broader if H-bonded. Free and H-bonded forms often simultaneously observed <i>In the same range:</i> OH st, $\equiv\text{CH}$ st, H_2O
NH_3^+ st	3000–2000 3000–2700	Medium, broad, highly structured Major maximum, comb: ≈ 2000
NH_2^+ st	3000–2000 3000–2700	Medium, broad, highly structured Major maximum
NH^+ st	3000–2000 2700–2250	Medium, broad, highly structured Major maximum <i>In the same range:</i> OH st, NH st, CH st, SH st, PH st, SiH st, BH st, $\text{X}=\text{Y}=\text{Z}$ st, $\text{X}\equiv\text{Y}$ st
NH_2 δ	1650–1590	Medium or weak
NH δ	1650–1550	Weak
NH_3^+ δ	1600–1460	Medium, often more than one band; weak in aliphatic amines
NH_2^+ δ	1600–1460	Medium, often more than one band; weak in aliphatic amines
NH^+ δ	1600–1460	Medium, often more than one band; weak in aliphatic amines
C–N st	1400–1000	Medium, of no practical significance
NH_2 δ	850–700	Medium or weak; 2 bands in primary amines
NH δ	850–700	Medium or weak
P–N–C st	1110–930, 770–680	

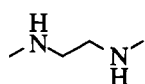
N

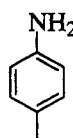
Examples (ν in cm^{-1})

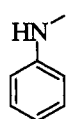
$\text{CH}_3\text{-NH}_2$ 3470
 3360
 1622

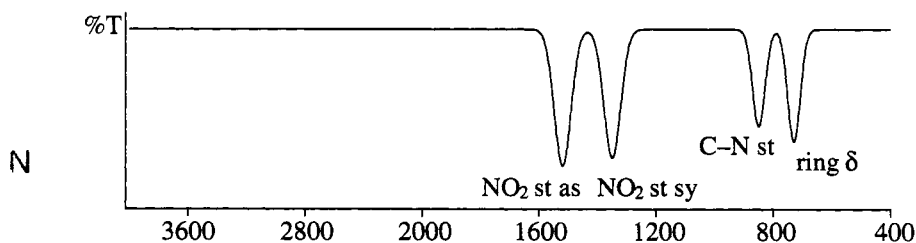
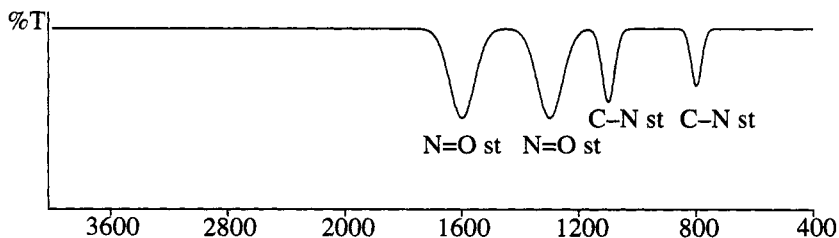
 3357
 3278
 3200 sh
 1605

 3356
 3274
 3175
 1650

 3279

 3487
 3405

 3416
 3386
 1322
 1266

6.9.2**Nitro and Nitroso Compounds****Nitro Compounds****Nitroso Compounds**

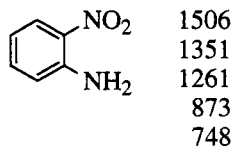
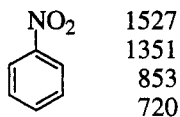
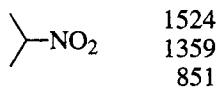
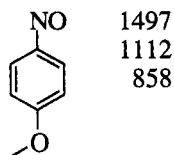
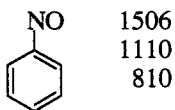
Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
NO₂ st as	1660–1490	Very strong, of medium width
	<i>Subranges:</i>	
	1660–1625	O–NO ₂ , nitrates
	1570–1540	C–NO ₂ , al nitro compounds
	1560–1490	C–NO ₂ , ar nitro compounds
NO₂ st sy	1630–1530	N–NO ₂ , nitramines
	1390–1260	Strong, of medium width
	<i>Subranges:</i>	
	1285–1270	O–NO ₂ , nitrates
	1390–1340	C–NO ₂ , al nitro compounds
	1360–1310	C–NO ₂ , ar nitro compounds; often 2 bands
	1315–1260	N–NO ₂ , nitramines
	<i>In nitrates also:</i>	
	≈870	N–O st, strong
	≈760	NO ₂ γ
Ring δ	≈700	NO ₂ δ
	760–705	Strong; modified deformation of aromatic ring
N=O st	1680–1450	Very strong, in monomers
	1420–1250	Very strong, in dimers
	<i>Subranges:</i>	
	1680–1650	O–NO (nitrites) trans; 1625–1610: cis
	1585–1540	C–NO, al C-nitroso compounds
	1510–1490	C–NO, ar C-nitroso compounds
	≈1450	N–NO, <i>N</i> -nitroso compounds
	<i>In nitrites also:</i>	
	3300–3200, ≈2500, 2300–2250	comb
	≈800	N–O st trans; cis: very weak
C–N st	≈600	O–NO δ trans; cis: ≈650
	≈850	C–NO, al C-nitroso compounds; coupled with other vibrations
	≈1100	C–NO, ar C-nitroso compounds
N–N st	≈1040	<i>N</i> -Nitroso compounds

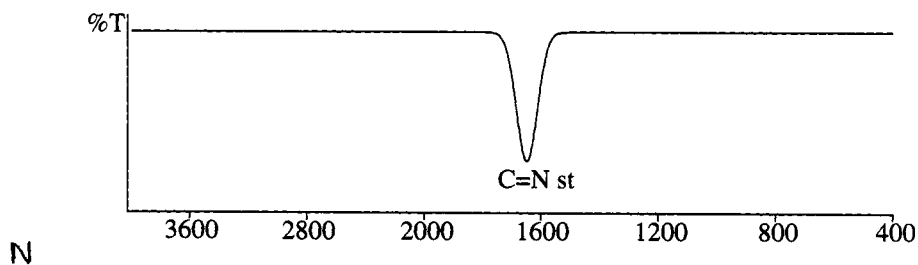
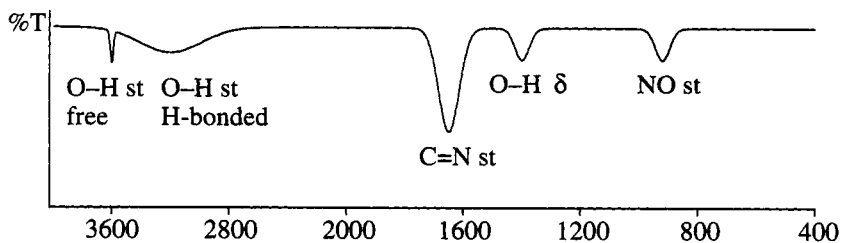
N

Examples (ν in cm^{-1})

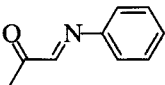
$\text{CH}_3\text{-NO}$ 1564
 842



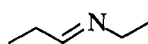
6.9.3 Imines and Oximes

Imines**Oximes**

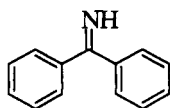
Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
C=N st	1690–1520	Generally strong
	<i>Subranges:</i>	
	≈ 1670	$\text{R}-\text{CH}=\text{N}-\text{R}'$ R, R': al
	≈ 1645	$\text{R}-\text{CH}=\text{N}-\text{R}'$ R or R': conjugated
	≈ 1630	$\text{R}-\text{CH}=\text{N}-\text{R}'$ R, R': conjugated
	≈ 1655	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \\ \text{R}'' \end{array}$ R, R', R'': al
	≈ 1645	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \\ \text{R}'' \end{array}$ R: conjugated
	≈ 1635	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \\ \text{R}'' \end{array}$ R, R': conjugated
	≈ 1555	 additional band: ≈ 1655 C=O
	≈ 1645	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{NH} \\ \diagup \\ \text{R}' \end{array}$ R, R': al
	≈ 1625	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{NH} \\ \diagup \\ \text{R}' \end{array}$ R, R': conjugated
	1685–1580	$\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \\ \text{H}_2\text{N} \end{array}$ Additional band at 1540–1515 in: $\begin{array}{c} \text{R} \\ \diagdown \\ \text{C}=\text{N} \\ \diagup \\ \text{RHN} \end{array}$
	1670–1600	$\text{CH}=\text{N}-\text{N}=\text{CH}$
	1690–1645	$\begin{array}{c} \text{RO} \\ \diagdown \\ \text{C}=\text{NH} \\ \diagup \\ \text{RO} \end{array}$ Additional bands: NH st: ≈ 3300 , C–O st: ≈ 1325 , ≈ 1100
	1680–1635	$\begin{array}{c} \text{RO} \\ \diagdown \\ \text{C}=\text{NH}_2^+ \\ \diagup \\ \text{RO} \end{array}$ Additional bands: NH_2^+ st: ≈ 3000 , NH_2^+ δ : 1590–1540
	2050–2000	$\text{C}=\text{C}=\text{N}$; Ketimines, very strong, sometimes doublet
	1580–1520	Quinone oximes: C=O st 1680–1620
	1685–1650	Aliphatic oximes
	1645–1650	Aromatic oximes
	1690–1645	$\text{O}-\text{C}=\text{N}$
	1640–1605	$\text{S}-\text{C}=\text{N}$
	1640–1580	$\text{S}-\text{S}-\text{C}=\text{N}$
OH st	3600–2700	Strong
	<i>Subranges:</i>	
	≈ 3600	Free
	3300–3100	H-bonded, broad
	$\geq \approx 2700$	Quinone oximes, more than one band
OH δ	1475–1315	Of no practical significance
N–O st	1050–400	Of no practical significance

N

Examples (ν in cm^{-1})

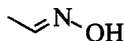
1667



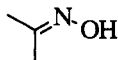
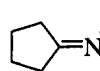
1603



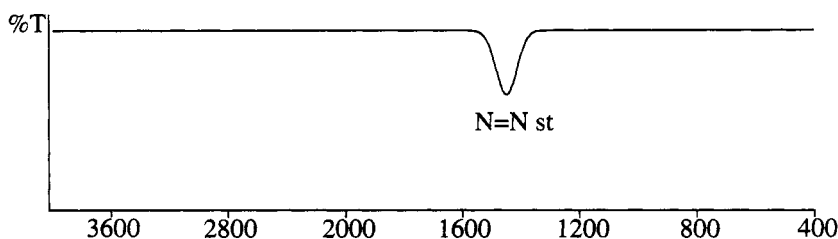
1637



1675

1672 (solid)
1662 (gas)

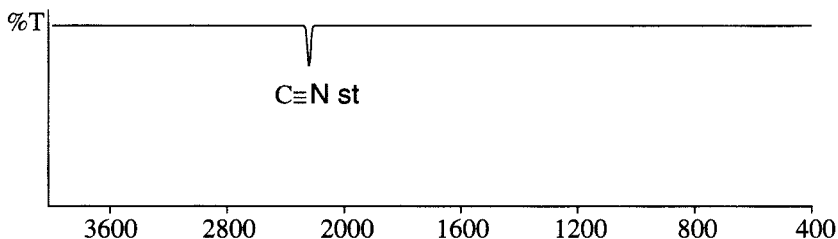
1684

6.9.4
Azo Compounds**Typical Ranges** (ν in cm^{-1})

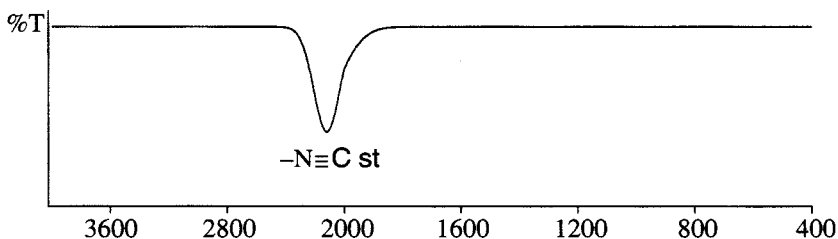
Assignment	Range	Comments
N	N=N st	1500–1400 Very weak, missing in compounds of high symmetry
	1480–1450	 st as st sy
	1335–1315	
	≈1450	
	≈1050	
	1410–1175	 Dimers of C-nitroso compounds
	Subranges: 1290–1175 Aliphatic <i>trans</i> 1425–1385, Aliphatic <i>cis</i> 1345–1320 1300–1250 Aromatic <i>trans</i> ≈1410, ≈1395 Aromatic <i>cis</i>	

6.9.5 Nitriles and Isonitriles

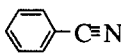
Nitriles



Isonitriles




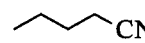
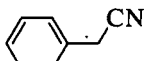
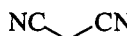
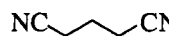
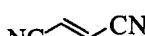
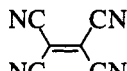
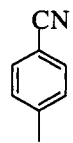
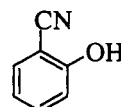
Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
$\text{C}\equiv\text{N st}$	2260–2240	Medium to strong, sharp; for $\text{O}-\text{CH}_2-\text{C}\equiv\text{N}$, $\text{N}-\text{CH}_2-\text{C}\equiv\text{N}$: of low intensity or absent
	<i>Beyond normal range:</i>	
	2240–2215	$\text{C}=\text{C}-\text{C}\equiv\text{N}$
	2240–2215	 $\text{C}\equiv\text{N}$
	2240–2230	$\text{XC}-\text{C}\equiv\text{N}$ X: Cl, Br, I
	≈ 2275	$-\text{CF}_2-\text{C}\equiv\text{N}$
	2225–2175	$\text{N}^+-\text{C}\equiv\text{N}^- \longleftrightarrow \text{N}^+=\text{C}=\text{N}^-$
	2210–2185	$>\text{N}-\text{C}=\text{C}-\text{C}\equiv\text{N}$
	2200–2070	$\text{C}\equiv\text{N}^-$
$-\text{N}^+\equiv\text{C}^-$	2150–2110	Strong

N

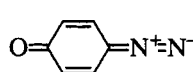
Assignment	Range	Comments
$\text{--N}^+\equiv\text{N}$	2310–2130	Medium, frequency depends on anion
<i>In the same range: C\equivC st, X=Y=Z st as, NH$^+$ st, PH st, POH st, SiH st, BH st</i>		

Examples (ν in cm^{-1})

	2222		2235		2252
	2273		2235		2252
	2257 2222		2245		2220
NaCN, KCN	2080–2070	AgCN	2178	NH $_2$ -CN	2268

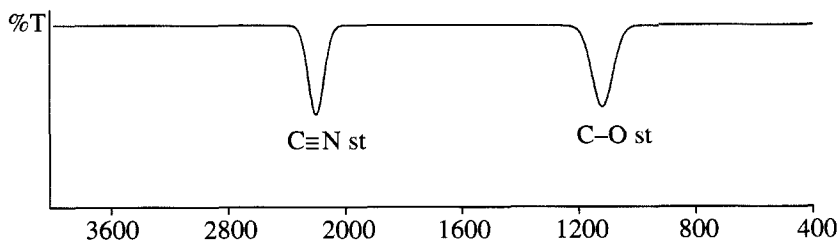
6.9.6**Diazo Compounds**

N

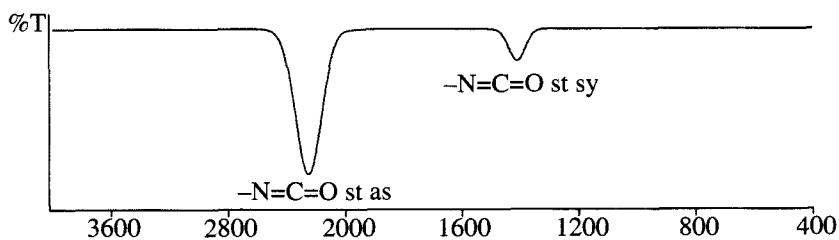
Assignment	Range	Comments
$\text{N}^+\equiv\text{N}$ st	2310–2130	Medium, frequency depends on anion
$\text{C}=\text{N}^+=\text{N}^-$	2050–2010	Very strong
<i>Subranges:</i>		
	2050–2035	R-CH=N $^+$ =N $^-$ R: al or ar
	2035–2010	R $_2$ -C=N $^+$ =N $^-$ R: al or ar
<i>Beyond normal range:</i>		
	2100–2050	R-CO-C=N $^+$ =N $^-$ C=O st \approx 1645 (R: al) C=O st \approx 1615 (R: ar) C=N $^+$ =N $^-$ st sy: \approx 1350, strong
	2180–2010	 C=O st 1655–1560

6.9.7 Cyanates and Isocyanates

Cyanates



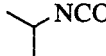


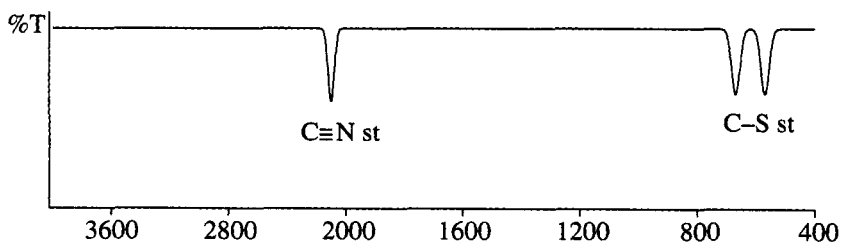
Isocyanates



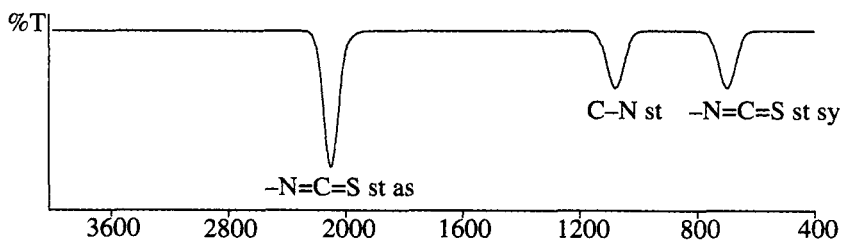
Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
OC≡N st	2260–2130	Medium to strong
	2220–2130	(OC≡N) ⁻
	1335–1290	(OC≡N) ⁻ st sy
C–O st	1200–1080	Strong
N=C=O st as	2280–2230	Strong, sharp
	≈2300	–CF ₂ NCO
N=C=O st sy	1450–1380	Weak
	<i>Beyond normal range:</i>	
	2220–2130	(N=C=O) ⁻

N

Examples (ν in cm^{-1}) CH_3NCO 2265 NCO 2280 NCO 2270 NCO 2256
(1629 $\text{C}=\text{C}$) NCO 2267 NCO 2246**6.9.8****Thiocyanates and Isothiocyanates****Thiocyanates**

N

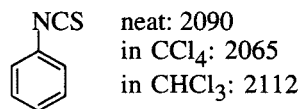
Isothiocyanates

Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
SC\equivN st	2170–2130 2090–2020	Medium, sharp (SC \equiv N) ⁺
C–S st	750–550	Often doublet
N=C=S st as	2200–2050	Very strong, generally doublet, Fermi resonance
N=C=S st sy	950–650 \approx 950 700–650	al –N=C=S ar –N=C=S
	<i>Beyond normal range:</i> 2090–2020	(N=C=S) ⁺
C–N st	1090–1075	

Examples (ν in cm^{-1})

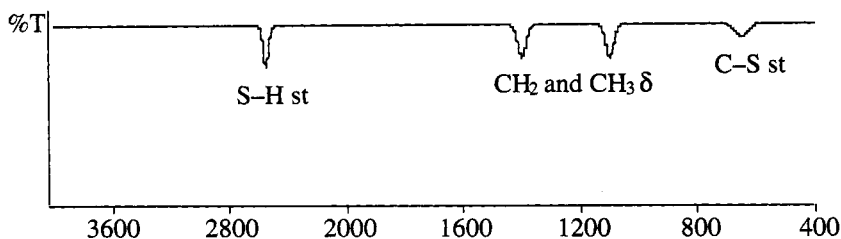
CH ₃ NCS	neat:	in CCl ₄ :		NCS	2173 2097 2068
	2206	2221			
	2114	2106			
		2077			



N

6.10 Sulfur-Containing Functional Groups

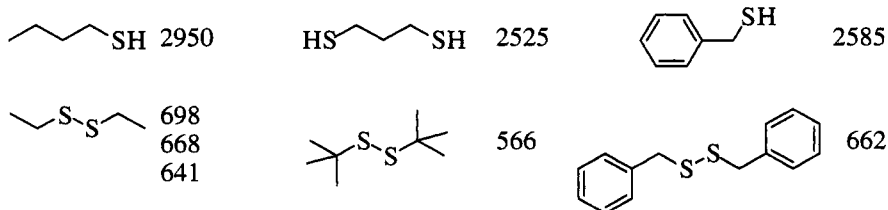
6.10.1 Thiols and Sulfides



Typical Ranges (ν in cm^{-1})

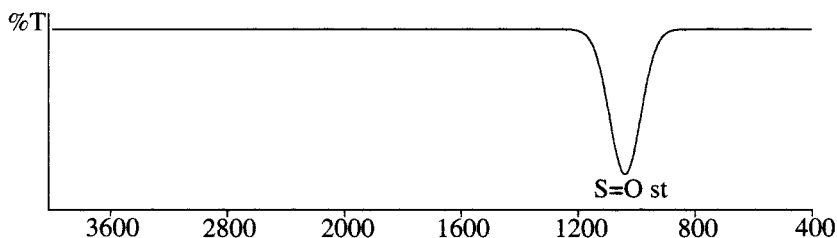
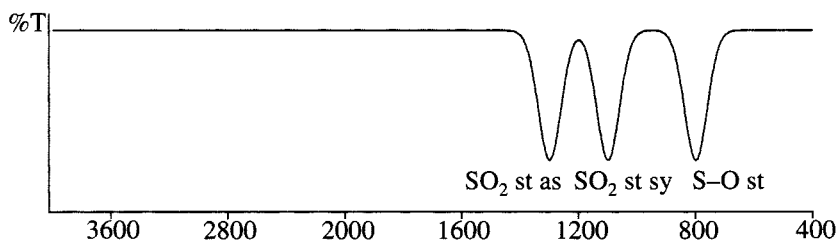
Assignment	Range	Comments
S-H st	2600–2540	Often weak, narrow
S-H δ	915–800	Weak, of no practical significance
C-S st	710–570	Weak, broad, of no practical significance
S-S st	≈ 500	Weak, of no practical significance
Also:	≈ 2880	(S-)CH ₃ st as
	≈ 2860	(S-)CH ₂ st as
	≈ 1430	(S-)CH ₃ δ as
	1330–1290	(S-)CH ₃ δ sy
	≈ 1425	(S-)CH ₂ δ
	815–755	S-F st, strong
	≈ 630	S-N st in S-N=O
	725–550	S-C in S-C \equiv N, often doublet

Examples (ν in cm^{-1})




6.10.2

Sulfoxides and Sulfones

Sulfoxides*Sulfones**Typical Ranges (ν in cm^{-1})*

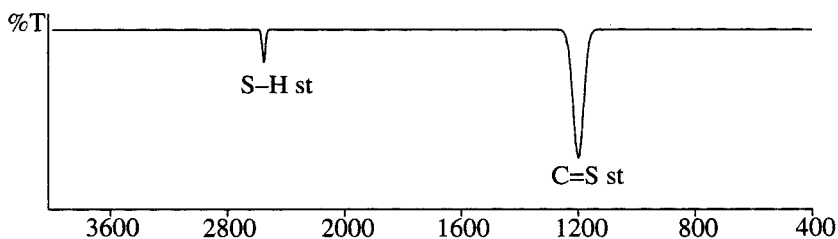
Assignment	Range	Comments
S=O st	1225–980	Strong, sometimes multiple bands
<i>Subranges:</i>		
	1060–1015	R–SO–R
	≈1100	R–SO–OH
		S–O st 870–810 OH st free ≈3700, H-bonded ≈2900, ≈2500
	≈1135	R–SO–OR
	1225–1195	RO–SO–OR
	≈1135	R–SO–Cl
	≈1030, ≈980	R–SO₂⁻
	≈1100, ≈1050	R=SO
		N=SO: ≈1250, ≈1135

S

Assignment	Range	Comments
 st as st sy	1420–1000	Very strong
<i>Subranges:</i>		
	1370–1290, 1170–1110	R–SO ₂ –R
	1375–1350, 1185–1165	R–SO ₂ –OR
	≈1340, ≈1150	R–SO ₂ –SR
	1415–1390, 1200–1185	RO–SO ₂ –OR
	1365–1315, 1180–1150	R–SO ₂ –N
		N–H st: 3330–3250; N–H δ: ≈1570; S–N st: 910–900
	1410–1375, 1205–1170	R–SO ₂ –hal
	1355–1340, 1165–1150	R–SO ₂ –OH
		O–H st, H-bonded: ≈2900, ≈2400 hydrated: 2800–1650, broad
	1250–1140, 1070–1030	R–SO ₃ [–]
	1315–1220, 1140–1050	RO–SO ₃ [–]
S–O st	870–690	Of variable intensity, weak in sulfites

6.10.3

Thiocarbonyl Derivatives

*Typical Ranges (ν in cm^{-1})*

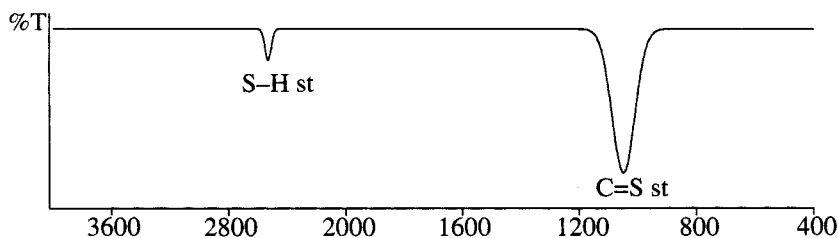
Assignment	Range	Comments
C=S st	1275–1030	Strong, narrow
	<i>Subranges:</i>	
	1075–1030	Thioketones
	1210–1080	Thioesters
	≈1215	Dithioacids
	1125–1075	Thioacid fluoride
	1100–1065	Thioacid chloride
	1140–1090	Thioamides and thiolactams
<i>Also:</i>	750–580	P=S st

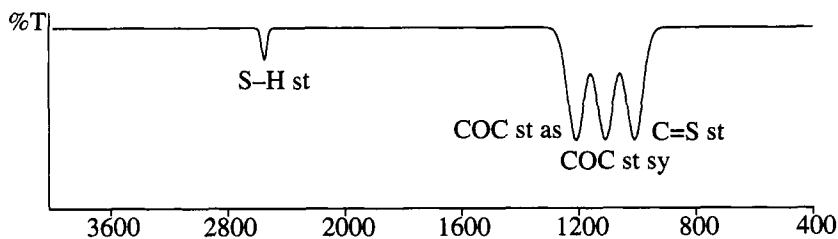
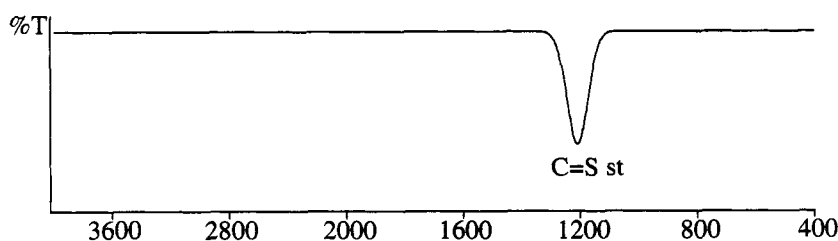
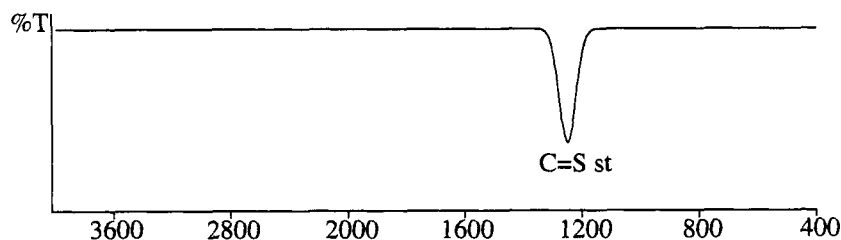
SH st: ≈2550
SH δ: ≈860
perfluorinated: 1130–1105
perchlorinated: 1100–1075
C–N st: 1535–1520
NH δ: 1380–1300

S

6.10.4

Thiocarbonic Acid Derivatives

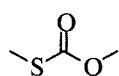
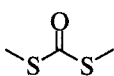
Trithiocarbonates

Xanthates**Thiocarbonates****Thioureas**

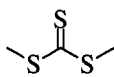
S

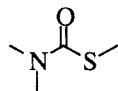
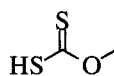
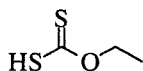
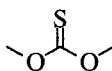
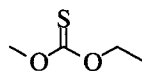
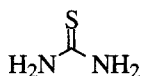
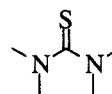
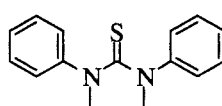
Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments	
S-H st	2560–2510	Weak, narrow	trithiocarbonates
	2600–2500	Weak, narrow	xanthates
C=S st	1100–1020	Very strong	trithiocarbonates
	1070–1000	Strong	xanthates
	1250–1180	Strong	thiocarbonates
	1400–1100	Strong	thioureas
COC st as	1260–1140	Strong	xanthates
COC st sy	1150–1090	Strong to medium	xanthates

Examples (ν in cm^{-1})
 in CCl_4 :
1719

 in CCl_4 :
1653

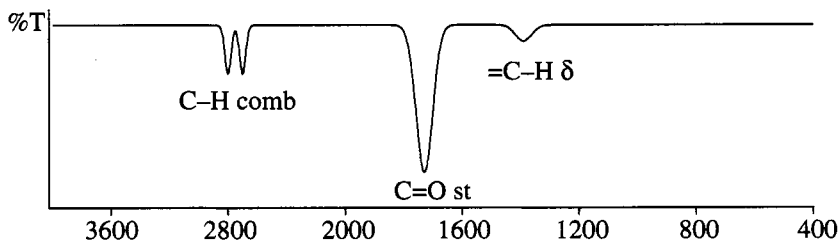
 in CCl_4 :
1757

 in CCl_4 :
1718
1677
1640

 neat:
1076

 solid:
1058
in CCl_4 :
1083
1079

 in CCl_4 :
1662

 gas:
2593
2548
neat:
2470

 in CS_2 :
2562
2522

 solid:
1212

 solid:
1234

 solid:
1400

 solid:
1130

 solid:
1131

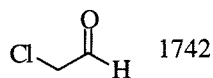
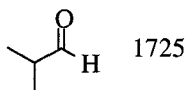
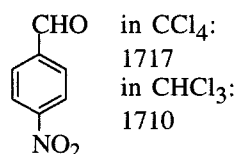
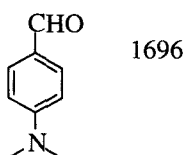
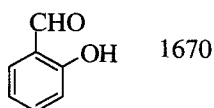
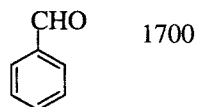
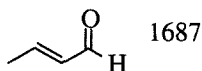
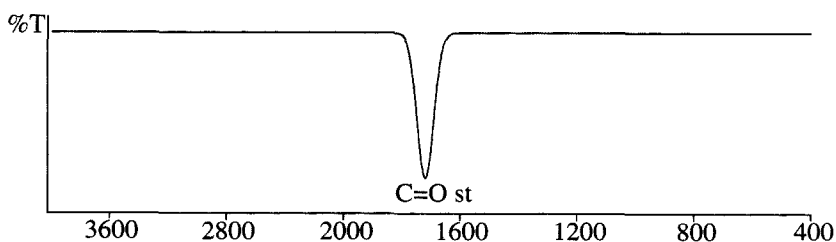
6.11 Carbonyl Compounds

6.11.1 Aldehydes



Typical Ranges (ν in cm^{-1})



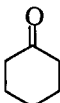
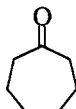
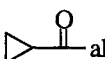
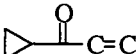
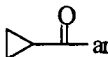
Assignment	Range	Comments
C-H comb	2900-2800	Weak, Fermi resonance with C-H δ at \approx 1390
	2780-2680	
		For extreme position of C-H δ only one band
	<i>Subranges:</i>	
	2830-2810, 2720-2690	Aliphatic
	2830-2810, 2750-2720	Aromatic, for <i>o</i> -substitution often higher
	<i>In the same range:</i> cyclohexanes at \approx 2700, weak	
C=O st	1765-1645	Strong
C=X	<i>Subranges:</i>	
	1740-1720	Aliphatic
	1765-1730	α -Halogenated aliphatics
	1710-1685	Aromatic
	1695-1660	α,β -Unsaturated aromatic
	1670-1645	With intramolecular H bonds
C-H δ	1390	Weak, of no practical significance

Examples (ν in cm^{-1})CH3CHO 1748CCl3CHO 1760**6.11.2
Ketones****Typical Ranges** (ν in cm^{-1})

Assignment	Range	Comments
C=O st	1775–1650	Strong
	<i>Subranges:</i> ≈ 1715	Aliphatic, branching at α -position causes shift to lower frequencies:
		≈ 1695 ≈ 1685
	≈ 1775 –1705	Cyclic, ν decreases with increasing ring size

[contd.]





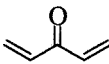
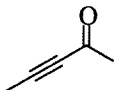
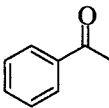
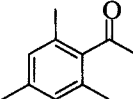
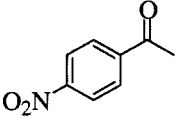
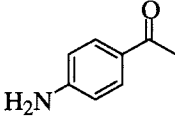
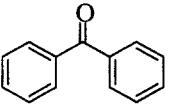
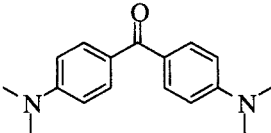
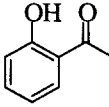

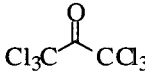
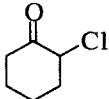
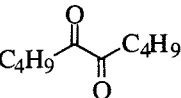


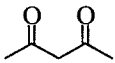
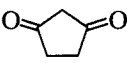
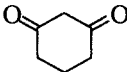
C=X

Assignment	Range	Comments																
		<div> ≈1775</div> <div> ≈1750</div>																
		<div> ≈1715</div> <div> ≈1705</div>																
Conjugated:	≈1675	α,β-Unsaturated, often 2 bands (rotational isomers)																
	1650–1600	C=C st																
	≈1695	 al																
	≈1665	α,β;γ,δ-Unsaturated; α,β;α',β'-unsaturated																
	≈1670	 C=C																
	≈1690	Aryl ketones																
	≈1675	 ar																
	≈1665	Diaryl ketones, with N or O in <i>p</i> -position: down to ≈1600																
α-Halogenated ketones:	Shifted toward higher wavenumbers depending on dihedral angle ϕ between C=O and C-hal; largest effect for $\phi = 0^\circ$, no effect for $\phi = 90^\circ$																	
	Maximal shifts:	<table><tr><td>α-chloro</td><td>≈25</td><td>α-bromo</td><td>≈20</td></tr><tr><td>α,α-dichloro</td><td>≈45</td><td>α-iodo</td><td>≈0</td></tr><tr><td>α,α'-dichloro</td><td>≈45</td><td>α,α-difluoro</td><td>≈60</td></tr><tr><td></td><td></td><td>perfluoro</td><td>≈90</td></tr></table>	α-chloro	≈25	α-bromo	≈20	α,α-dichloro	≈45	α-iodo	≈0	α,α'-dichloro	≈45	α,α-difluoro	≈60			perfluoro	≈90
α-chloro	≈25	α-bromo	≈20															
α,α-dichloro	≈45	α-iodo	≈0															
α,α'-dichloro	≈45	α,α-difluoro	≈60															
		perfluoro	≈90															
α-Diketones:	≈1720	Aliphatic																
	≈1775, ≈1760	Aliphatic 5-ring																
	≈1760	Aliphatic 6-ring																
	≈1730																	
	≈1675	Aliphatic enolized, C=C st: ≈1650																
	≈1680	Aromatic																
	≈1675	<i>o</i> -Quinones, with <i>peri</i> -OH: ≈1675, ≈1630																
β-diketones:	≈1720	Keto form, sometimes doublet																
	≈1650	Enol form																
	≈1615	Enol with intramolecular H bonds, C=C st: ≈1600 strong																

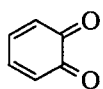
C = X

Assignment	Range	Comments
γ -diketones:	≈ 1675	As monoketones <i>p</i> -Quinones, with <i>peri</i> -OH: ≈ 1675 , ≈ 1630 ; C=C st: ≈ 1600
C=C=O st as	2155–2130	Very strong

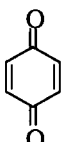
Examples (ν in cm^{-1})

 1691	 1697	 \rightleftharpoons  <i>s-trans</i> 1690 <i>s-cis</i> 1707
 1672 1660	 1678 (2222)	 1692
 1701	 1702	 1676
 1664	 1639	 1648
 1752 1726 (rotamers)	 1780 1751	 1722
 1710	 1700 1655	 1735
 1724 (keto form) 1608 (enol form)	 1755 1725 1635 1590	 1630 1607

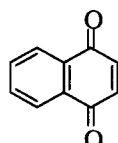
C = X



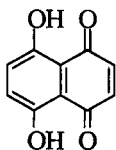
1669



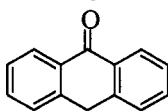
1669



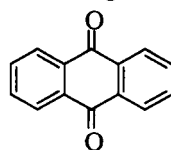
1675



1623



1662

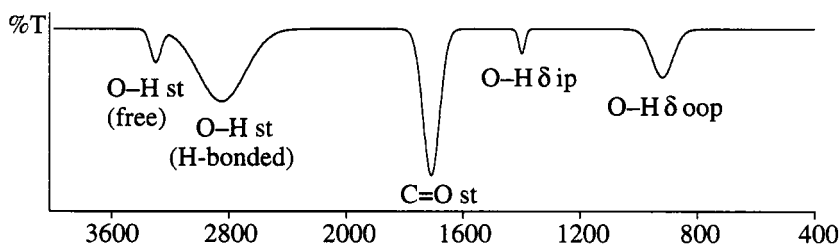


1678

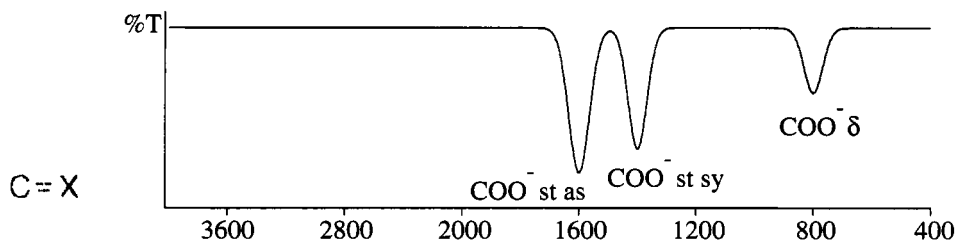
6.11.3

Carboxylic Acids

Carboxylic Acids



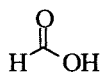
Carboxylate Anions



Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
COO-H st	3550–2500	intensity variable
	<i>Subranges:</i>	
	3550–3500	Free, sharp, only in highly diluted solutions
	3300–2500	H-bonded, broad, often more than one band
	<i>In the same range also OH st, NH st, CH st, SiH st, SH st, PH st</i>	
C=O st	1800–1650	Strong
	1800–1740	Free (also in dicarboxylic acids)
	1740–1650	H-bonded (dimer, also in dicarboxylic acids)
	<i>Subranges for H-bonded C=O:</i>	
	1725–1700	al-COOH
	1715–1690	C=C-COOH
	1700–1680	ar-COOH
	1740–1720	hal-C-COOH
	1670–1650	Intramolecular H bond
OC-OH st,	1440–1210	Of no practical significance
C-OH δ		
OC-OH δ oop	960–880	Medium, generally broad (only in dimers), in the same range: =CH δ , ar CH δ , NH δ
(COO)⁻ st as	1610–1550	Very strong; in α -halogen carboxylates near the higher value, with more than one α -hal beyond the normal range; in polypeptides at ≈ 1575
(COO)⁻ st sy	1450–1400	Strong, of no practical significance, in polypeptides at ≈ 1470
(COO)⁻ δ	≈ 775	Formates, weak
	≈ 925	Acetates
	≈ 680	Benzoates
	≈ 600	CF ₃ COO ⁻

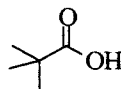
C=X

Examples (ν in cm^{-1})

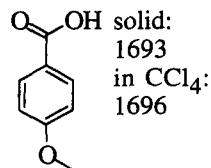
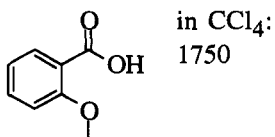
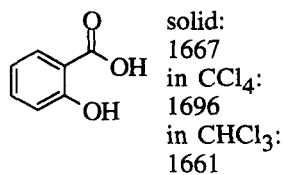
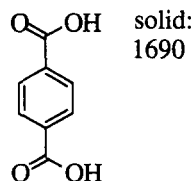
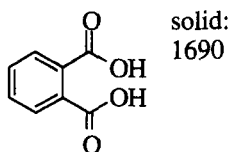
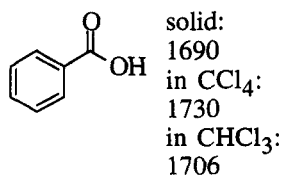
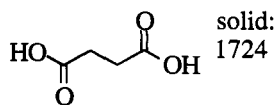
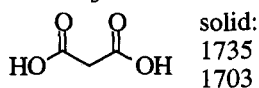
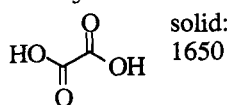
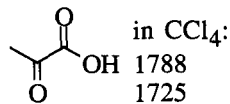
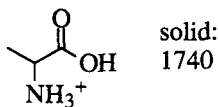
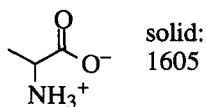
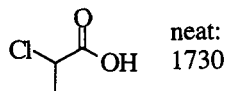
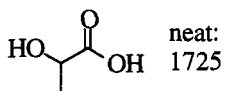
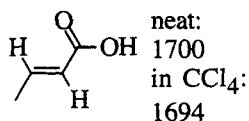
neat:
1727
in CCl₄:
1756
1724



neat:
1759
1718
in CCl₄:
1768
1717

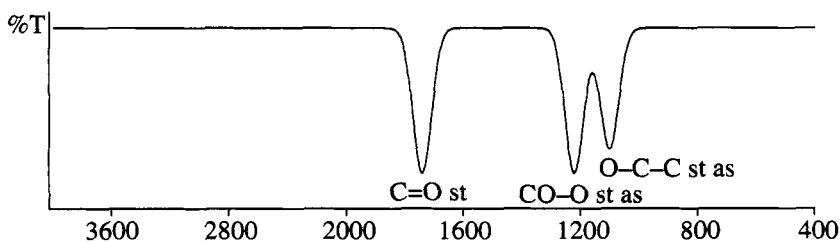


in CCl₄:
1704
solid:
1686











6.11.4

Esters and Lactones

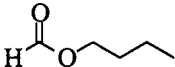
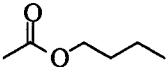
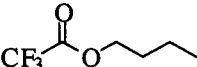
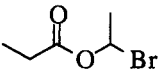
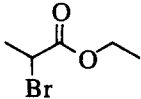
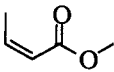
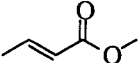
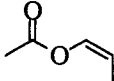
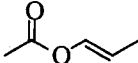
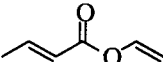
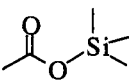
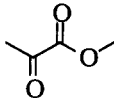
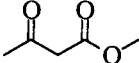
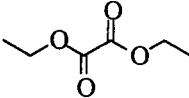
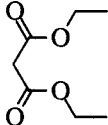
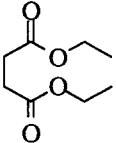
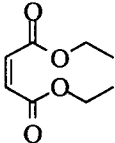
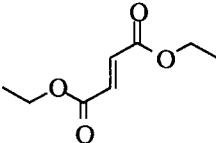
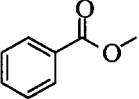
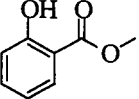
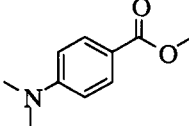
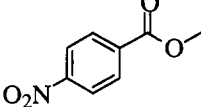
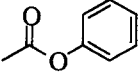
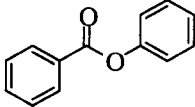
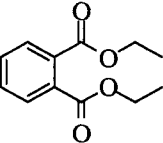
 $\text{C}=\text{X}$ 

Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
C=O st	1790–1650	Strong
	<i>Subranges:</i>	
	1750–1735	Aliphatic esters
<i>Conjugated esters:</i>	1730–1710	α,β -Unsaturated esters
	1730–1715	Aromatic esters
	1690–1670	With intramolecular H bonds
	1790–1740	α -Halogenated esters
	≈ 1760	Vinyl esters, C=C st: 1690–1650, strong
	≈ 1760	Phenol esters
	≈ 1735	Phenol esters of an aromatic acid
<i>Diesters:</i>		As the corresponding monoesters
<i>Keto esters:</i>	1755–1725	α -Keto esters, generally one band
	≈ 1750 (ketone)	β -Ketoesters, keto form
	≈ 1735 (ester)	
	≈ 1650	β -Ketoesters, enol form, C=C st: ≈ 1630 , strong
	$\approx 1740, \approx 1715$	γ -Ketoesters, pseudoesters: ≈ 1770
<i>Lactones:</i>	 ≈ 1840  ≈ 1770  ≈ 1800	
	 ≈ 1750 (additional band at ≈ 1780 if α -position free)  ≈ 1735	
	 ≈ 1760  ≈ 1720  ≈ 1730 (often doublet)	
C–O st	1330–1050	2 bands: st as, very strong and at higher frequency; st sy, strong, at lower frequency
C–O st as:	<i>Subranges:</i>	
	≈ 1185	Formates, propionates, higher aliphatic esters
	≈ 1240	Acetates
	≈ 1210	Vinyl esters, phenol esters
	≈ 1180	γ -Lactones, δ -lactones
	≈ 1165	Methyl esters of aliphatic acids
	<i>In the same range:</i> Strong bands for	
	C–F st, C–N st, N–O st, P–O st, C=S st, S=O st, P=O st, Si–O st, Si–H δ	

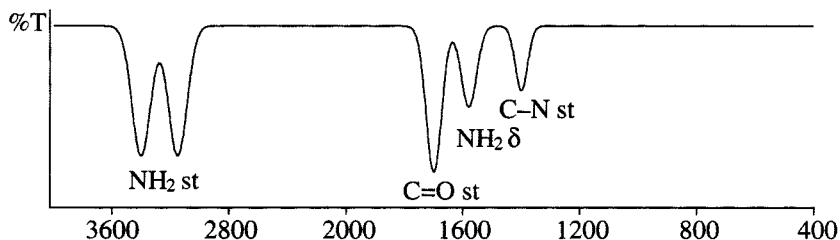
C = X

Examples (ν in cm^{-1})

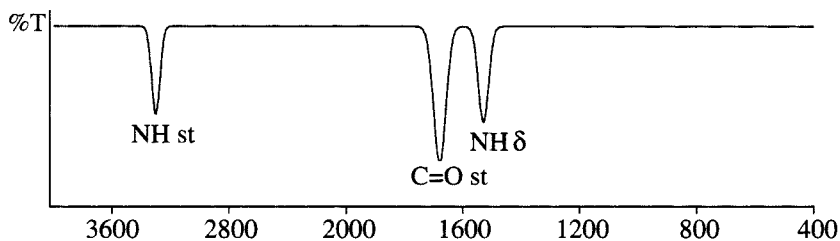
	1730		1743		1787
	1747		1743		1724
	1726		1758 (1690)		1752 (1675)
	1730 (1658) (1638)		1725		1725
	ester: 1704 ketone: 1690 enol: 1645		1774 1754		1760 1742
	1740		1734		1727
	1727		1684		1715
C=X					
	1737		1766		1743
	1746				

6.11.5 Amides and Lactams

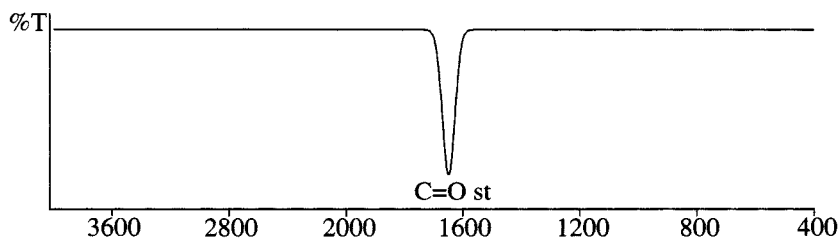
Primary Amides



Secondary Amides



Tertiary Amides

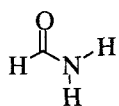


C = X

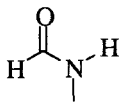
Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
N-H st	3500–3100	Medium, in primary amides two bands, in proteins multiplet
<i>Subranges:</i>		
	3500–3400	Free
	3350–3100	H-bonded
	$\approx 3350, \approx 3180$ In primary amides generally two bands	

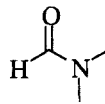
Assignment	Range	Comments
	≈3200, ≈3100	In lactams generally two bands
	≈3200	Monohydrazides
	≈3100	Dihydrazides
	≈3250	Imides
	<i>In the same range:</i> OH st, ≡CH st (≈3300, sharp), H ₂ O	
C=O st (amide I)	1740–1630	Generally strong
	<i>Subranges:</i>	
	≈1690	NH ₂ C=O free amides, H-bonded: ≈1650
	≈1685	NHC=O free amides, H-bonded: ≈1660
	≈1650	NC=O free amides, H-bonded: ≈1650
	≈1745	4-Ring lactams
	≈1700	5-Ring lactams
	≈1650	6-, 7-Ring lactams
	≈1670	Monohydrazides
	≈1600	Dihydrazides
	1740–1670	Imides
	≈1750, 1700	5-Ring imides, 2 bands
	1655–1630	Polypeptides
	≈1690	Isocyanurates, with aromatic substitution at ≈1770
	≈1720	
	1755 sh	Trifluoroacetamides
NH δ and N–C=O st sy (amide II)	1630–1510	Generally strong, absent in lactams
	<i>Subranges:</i>	
	≈1610	NH ₂ C=O free, H-bonded: ≈1630
	≈1530	NHC=O, H-bonded: ≈1540
	1560–1510	Polypeptides
	≈1555	Trifluoroacetamides
C=N st (?)	≈1400	NH ₂ C=O
	≈1250	NHC=O
	≈1330	Lactams
NH δ ip	≈1150	NH ₂ C=O
	≈1465	Lactams
NH δ oop	750–600	NH ₂ C=O
	≈700	NHC=O
	≈800	Lactams

Examples (ν in cm^{-1})

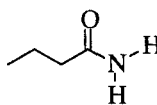
neat:
1672
in CHCl_3 :
1709



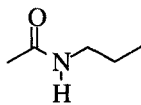
neat:
1672



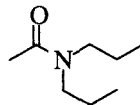
neat:
1670
in CHCl_3 :
1673



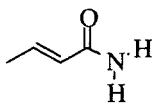
solid:
1631
in CHCl_3 :
1679



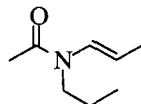
in CCl_4 :
1690



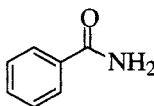
in CCl_4 :
1647



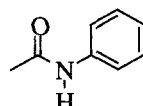
solid:
1677



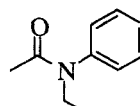
in CS_2 :
1675
1650



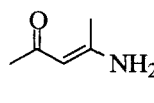
solid:
1656
in CHCl_3 :
1678



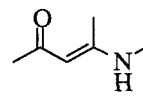
solid:
1658
in CHCl_3 :
1691
in CCl_4 :
1705



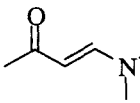
in CCl_4 :
1667



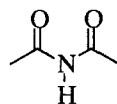
neat:
1700
1625
1540



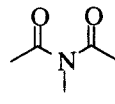
solid:
1628
1595



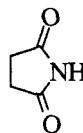
solid:
1631
1584



solid:
1734
1505

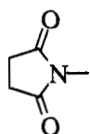


solid:
1736
1706
1689

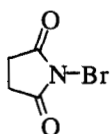


solid:
1771
1698
in CCl_4 :
1753
1727

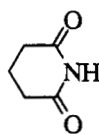
C=X



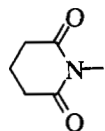
solid:
1760
1690
in CCl_4 :
1721
1705



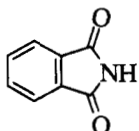
in CHCl_3 :
1783
1733



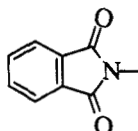
in CCl_4 :
1742
1730
1718



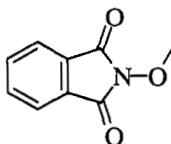
solid:
1718
1670
in CCl_4 :
1729,
1686



solid:
1774
1749
1724
in CHCl_3 :
1778
1735



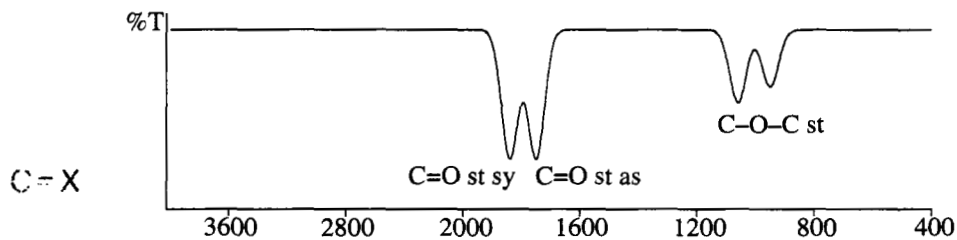
in CHCl_3
1772
1712



solid:
1790
1735

6.11.6

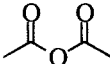
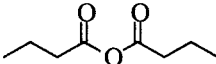
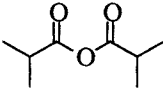
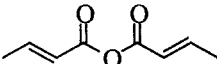
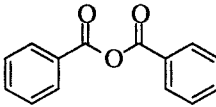
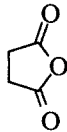
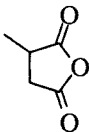
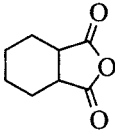
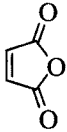
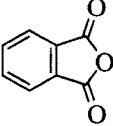
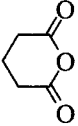
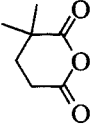
Acid Anhydrides



Typical Ranges (ν in cm^{-1})

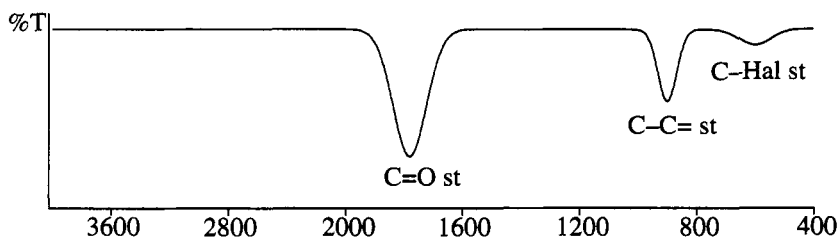
Assignment	Range	Comments
C=O st sy	1870–1770	Strong
C=O st as	1800–1720	Strong
<i>Subranges:</i>		
	$\approx 1820, \approx 1760$	Linear anhydrides, higher band stronger
	$\approx 1850, \approx 1775$	5-Ring, lower band stronger
	$\approx 1800, \approx 1760$	6-Ring, lower band stronger
C–O–C st	1300–900	Strong, several bands
	≈ 1040	Linear anhydrides
	≈ 920	Cyclic anhydrides

Examples (ν in cm^{-1})

	1825 1748		1810 1740 1045 1040		1803 1743
	1780 1725		1790 1727 1035 1015 995		1865 1782 920
	1859 1789		1845 1780		1850 1800 900
	1840 1810 1760 912		1802 1761		1802 1761

C=X

6.11.7 Acid Halides



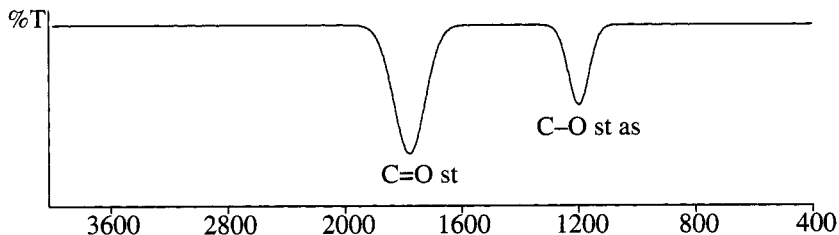
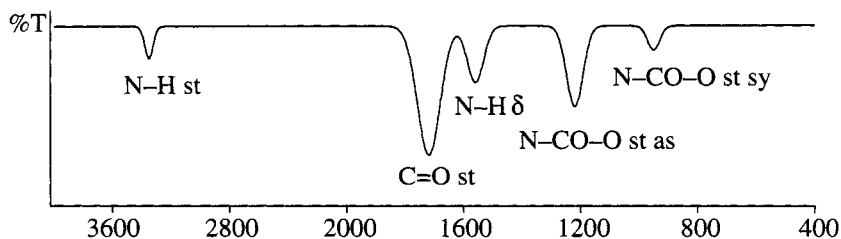
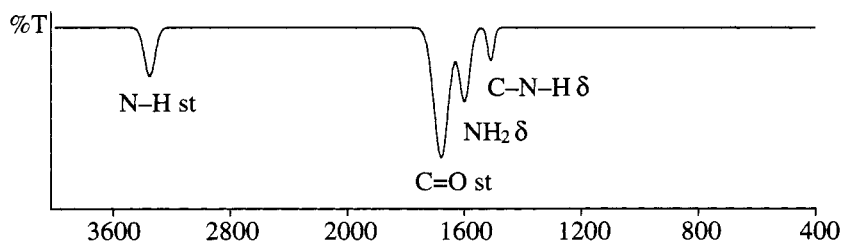
Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
C=O st	1820–1750	chlorides, strong, of narrow or medium width, for bromides and iodides at lower frequency
	1900–1870	fluorides, strong, of narrow or medium width, additional band at ≈ 1725 in aromatic acid chlorides and bromides
C-CO st	1000–800	1000–900 al, assignment uncertain
		900–800 ar, assignment uncertain
C-hal st	1200–500	1200–800 F
		750–550 Cl
		700–500 Br
		600–500 I

C = X

6.11.8

Carbonyl Acid Derivatives

Carbonyl Acid Derivatives*Carbamates**Ureas*

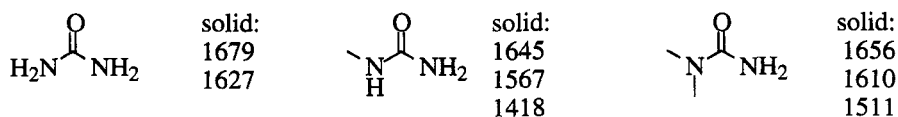
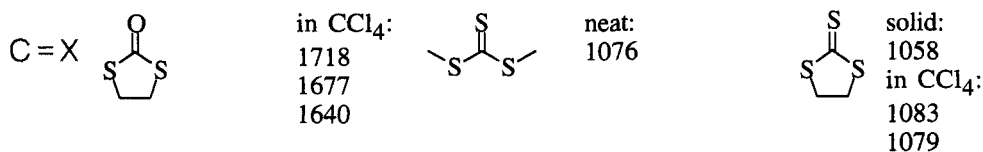
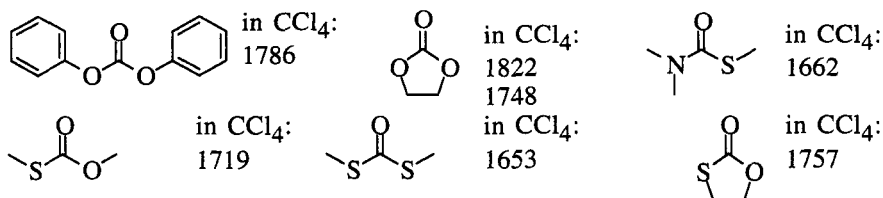
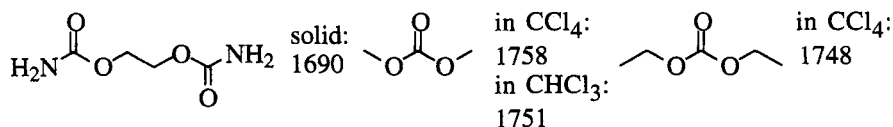
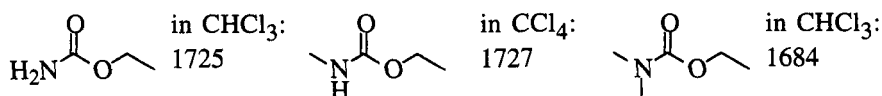
C = X

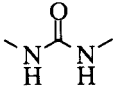
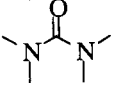
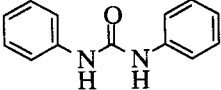
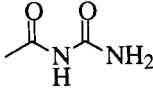
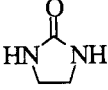
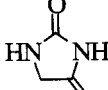
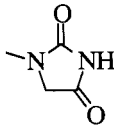
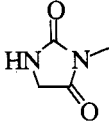
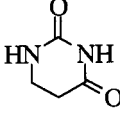
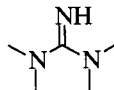
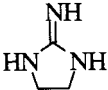
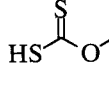
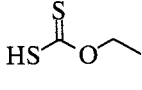
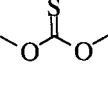
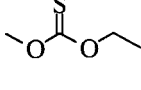
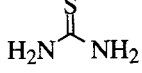
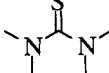
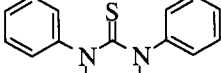
Typical Ranges (ν in cm⁻¹)

Assignment	Range	Comments
C=O st	1820–1740	Strong carbonyl acid derivatives
	1750–1680	Strong carbamates
	1690–1620	Strong ureas
C–O st as	1260–1150	Strong carbonyl acid derivatives

Assignment	Range	Comments
N-H st	3500-3250	Medium, two bands for NH_2 , one for NH
	3500-3200	Medium, two bands for NH_2
N-H δ	1650-1500	Medium
NH_2 δ	1650-1600	Medium
N-CO-O st as	1270-1210	Medium
N-CO-O st sy	1050-850	Weak
C-N-H δ	1600-1500	Weak

Examples (ν in cm^{-1})

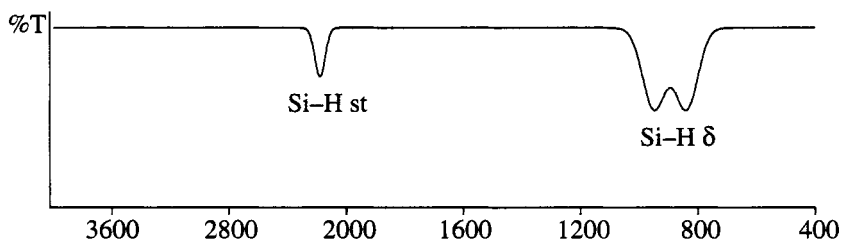


	solid: 1622 1580 1530 in CHCl ₃ : 1663 1548		solid: 1645 1560 1497 CHCl ₃ : 1675		solid: 1650
	solid: 1667 1634		in CCl ₄ : 1735 1718		solid: 1776 1697
	solid: 1712 1676		solid: 1748 1706		solid: 1767 1695
	neat: 1600		solid: 1767 1681 1621		gas: 2593 2548 neat: 2470
	in CS ₂ : 2562 2522		solid: 1212		solid: 1234
	solid: 1400		solid: 1130		solid: 1131

C=X

6.12 Miscellaneous Compounds

6.12.1 Silicon Compounds



Typical Ranges (ν in cm^{-1})

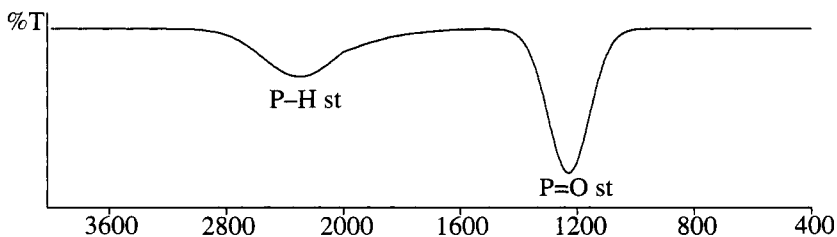
Assignment	Range	Comments
Si-H st	2250–2090	Medium
	<i>Subranges:</i>	
	2160–2090	$\text{R}_3\text{Si-H}$; also for R as H, for SiH_3 2 bands
	≈ 2250	hal-Si-H
	2220–2120	(Si-O)Si-H
Si-H δ	1010–700	Strong, broad, generally 2 bands
(Si-)CH₃ δ as	≈ 1410	Weak
(Si-)CH₃ δ sy	1275–1260	Very strong, sharp, typical for SiCH_3 , not split for $\text{Si}(\text{CH}_3)_2$
(Si-)CH₃ γ	860–760	
	≈ 765	SiCH_3
	$\approx 855, \approx 800$	$\text{Si}(\text{CH}_3)_2$
	$\approx 840, \approx 765$	$\text{Si}(\text{CH}_3)_3$
Misc. Si-O st	1110–1000, 900– <600	
	1110–1000, 850–800	Si-O-C
	1090–1030, < 650	Si-O-Si
	900–800	Si-OH
	3700–3200	Si-OH st
	≈ 1030	Si-OH δ

Assignment	Range	Comments
Si-C st	850–650	
Si-N st	1250–830	
	<i>Subranges:</i>	
	950–830	Si–N–Si
	≈3400	Si ₂ NH st
	950–830	N–Si–N
	1250–1100	Si–NH ₂
	≈3570, ≈3390	SiN–H ₂ st
	≈1540	Si–NH ₂ δ
Si-F st	980–820	
	<i>Subranges:</i>	
	920–820	Si–F
	945–870	Si–F ₂ , 2 bands
	980–860	Si–F ₃ , 2 bands
Si-Cl st	< 625	

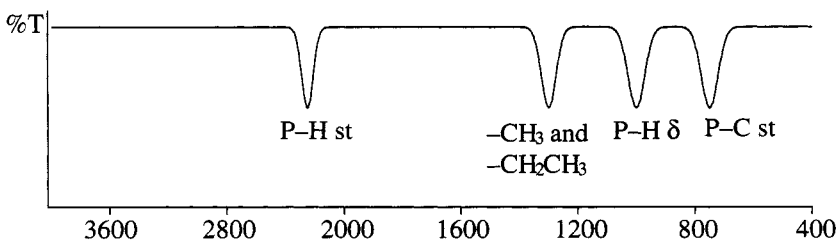
6.12.2

Phosphorus Compounds

Phosphorous Compounds



Phosphines



Misc.

Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
P-H st	2440–2275	Weak to medium, generally one band, in R_3PH^+ very broad
PO-H st	2700–2650	Weak, very broad
POH comb	2300–2250	Weak, very broad
	1740–1600	Additional band in $\text{O}=\text{P}-\text{OH}$ (dimer?)
P-O st	1260–855	
	<i>Subranges:</i>	
	1050–970, 830–740	P–O–C al st; strong and often weak for upper and lower band, respectively
	1260–1160	P–O–C ar st
	995–915	P(V)
	875–855	P(III)
	1100–940	P–OH st, broad, for $\text{P}(\text{OH})_2$ often two bands
	980–900	P–O–P st
P=O st	1300–960	Strong
	<i>Subranges:</i>	
	1190–1150	$\text{R}_3\text{P}=\text{O}$, also for R: H
	1265–1200	$\text{R}_2(\text{R}'\text{O})\text{P}=\text{O}$, also for R: H
	1280–1240	$\text{R}(\text{R}'\text{O})_2\text{P}=\text{O}$, also for R: H
	1300–1260	$(\text{RO})_3\text{P}=\text{O}$
	1220–1150	$\text{R}(\text{HO})_2\text{P}=\text{O}$
	1250–990	$\text{R}(\text{HO})\text{PO}_2^-$, more than one band
	1125–970, 1000–960	RPO_3^{2-}
	1205–1090	$\text{R}_2(\text{HO})\text{P}=\text{O}$
	1200–1090, 1090–995	R_2PO_2^-
	≈ 1250	$\text{RO}(\text{HO})_2\text{P}=\text{O}$
	1230–1210, 1030–1020	$\text{RO}(\text{HO})\text{PO}_2^-$
Misc.	1140–1050, 1010–970	ROPO_3^{2-}
	1250–1210	$(\text{RO})_2(\text{HO})\text{P}=\text{O}$
	1285–1120, 1120–1050	$(\text{RO})_2\text{PO}_2^-$
	1220–1170	$\text{R}(\text{RO})(\text{HO})\text{P}=\text{O}$
	1245–1150, 1110–1050	$\text{R}(\text{RO})\text{PO}_2^-$

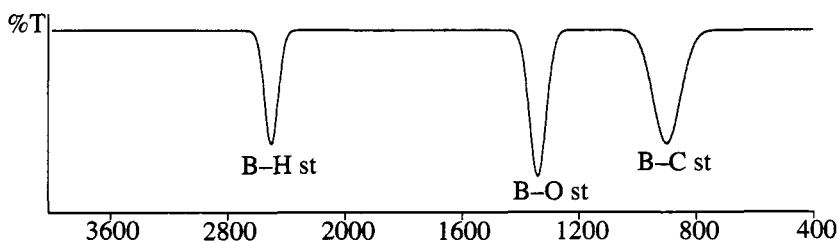
Assignment	Range	Comments
	1240–1205	$\begin{array}{c} \text{R} \quad \text{O} \quad \text{O} \quad \text{R} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{R}-\text{P}-\text{O}-\text{P}-\text{R} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \end{array}$
	1310–1260	$\begin{array}{c} \text{RO} \quad \text{O} \quad \text{O} \quad \text{OR} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{RO}-\text{P}-\text{O}-\text{P}-\text{OR} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \end{array}$
	≈ 1195	$\begin{array}{c} \text{HO} \quad \text{O} \quad \text{O} \quad \text{OH} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{R}-\text{P}-\text{O}-\text{P}-\text{OR} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \end{array}$
	≈ 1275	$\begin{array}{c} \text{RO} \quad \text{O} \quad \text{O} \quad \text{OR} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{R}_2\text{N}-\text{P}-\text{O}-\text{P}-\text{NR}_2 \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \end{array}$
	1265–1250	$\begin{array}{c} \text{R} \quad \text{O} \quad \text{O} \quad \text{R} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{RO}-\text{P}-\text{O}-\text{P}-\text{OR} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \end{array}$
	$\approx 1300, \approx 1240$	$\begin{array}{c} \text{RO} \quad \text{O} \quad \text{O} \quad \text{NR}_2 \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{RO}-\text{P}-\text{O}-\text{P}-\text{NR}_2 \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \end{array}$
	≈ 1250	$\begin{array}{c} \text{RO} \quad \text{O} \quad \text{O} \quad \text{OR} \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{HO}-\text{P}-\text{O}-\text{P}-\text{OH} \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \end{array}$
	≈ 1235	$\begin{array}{c} \text{R}_2\text{N} \quad \text{O} \quad \text{O} \quad \text{NR}_2 \\ \diagdown \quad \diagup \quad \diagdown \quad \diagup \\ \text{R}_2\text{N}-\text{P}-\text{O}-\text{P}-\text{NR}_2 \\ \diagup \quad \diagdown \quad \diagup \quad \diagdown \end{array}$
	1265–1240	$\text{R}_2(\text{X})\text{P}=\text{O}$, X: F, Cl, Br
	1365–1260	$\text{R}(\text{X})_2\text{P}=\text{O}$, X: F, Cl, Br
	1330–1280	$(\text{RO})_2(\text{X})\text{P}=\text{O}$, X: F, Cl, Br
	1365–1260	$\text{RO}(\text{X})_2\text{P}=\text{O}$, X: F, Cl, Br
P=N	1500–1170	
P–OH δ	≈ 1280	Weak, of no practical significance
P–C st	800–700	Intensity varies widely, of no practical significance
P–H δ	1090–910	Strong, for $(\text{RO})_2\text{HP}=\text{O}$ very strong
P–N–C st	1110–930, 770–680	
P=N–al st	1500–1230	
P=N–ar st	1390–1300	
P=N–C=O st	1370–1310	
P=N–PR₂ st	1295–1170	
P=S st	750–580	Intensity varies widely
P–S st	<600	
(P–)CH₃ δ sy	1310–1280	

Misc.

Assignment	Range	Comments
P-F st	905–760	
PF₂	1110–800	More than one band
P-Cl st	<600	

6.12.3

Boron Compounds

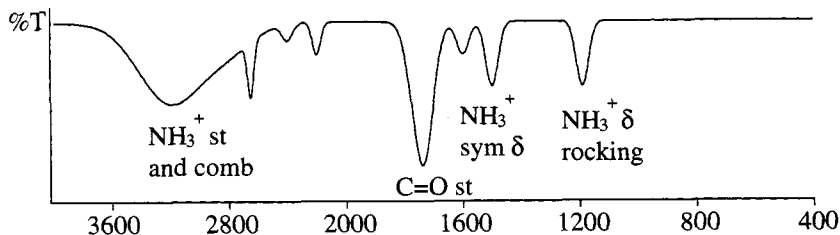


Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
B-H st	2640–2200	Strong
	2200–1540	B–H...B, more than one band
B-O st	1380–1310	Very strong
	≈1500	Haloboroxines
BO-H st	3300–3200	Very broad
B-N st	1550–1330	Very strong
B-C st	1240–620	Strong, 2 bands if substitution highly asymmetric
B-F st	1500–800	
B-Cl st	1100–650	

Misc.

6.13 Amino Acids



Typical Ranges (ν in cm^{-1})

Assignment	Range	Comments
N-H st	3400–2000	Generally strong, broad, very structured
O-H st		
	<i>Subranges:</i>	
	3100–2000	Zwitterions, distinct side band at 2200–2000
	3350–2000	Hydrochlorides
	3400–3200	Na^+ salts
NH_3^+ δ as	1660–1590	Weak, for hydrochlorides near the lower limit
NH_3^+ δ sy	1550–1480	Medium
COO^- st as	1760–1595	Strong
	<i>Subranges:</i>	
	≈ 1595	Zwitterions
	1755–1700	Hydrochlorides, in α -amino acids: 1760–1730
	≈ 1595	Na^+ salts

6.14

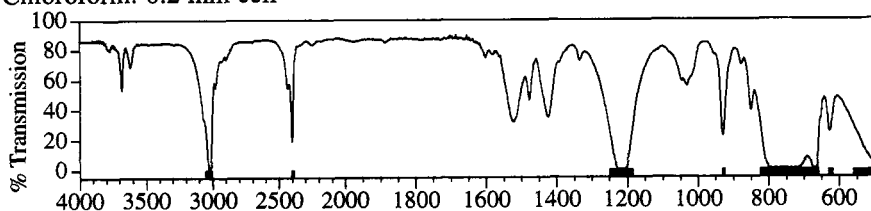
Solvents, Suspension Media, and Interferences

6.14.1

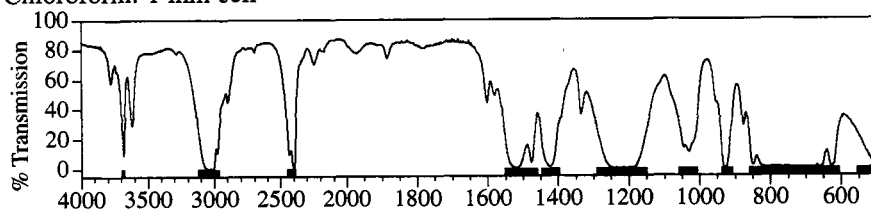
Infrared Spectra of Common Solvents

The low transmission in regions where the solvent absorbs may lead to artifacts. For the interpretation of spectra, these regions should be disregarded. In the following, they are indicated by bars.

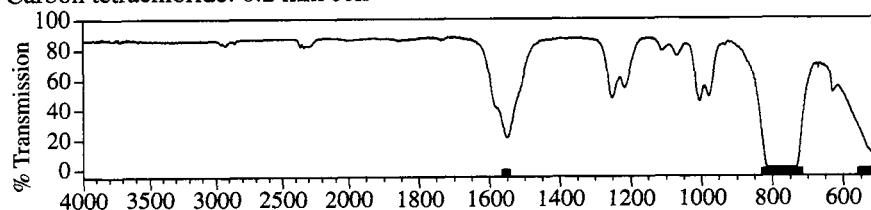
Chloroform: 0.2 mm cell



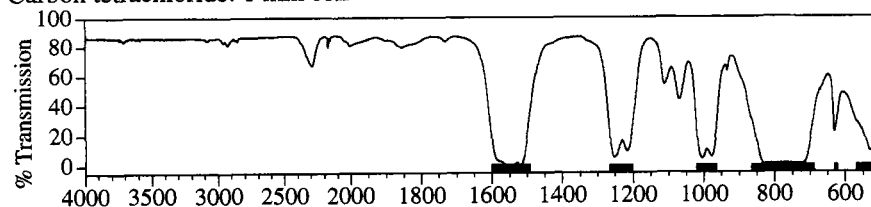
Chloroform: 1 mm cell



Carbon tetrachloride: 0.2 mm cell

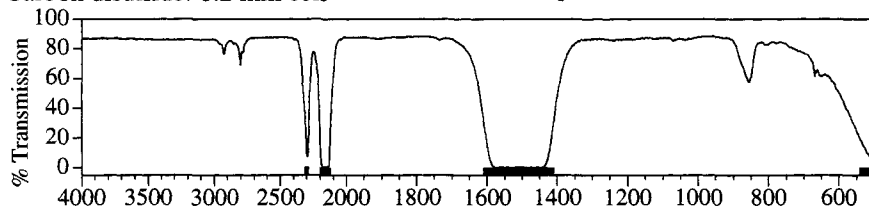


Carbon tetrachloride: 1 mm cell

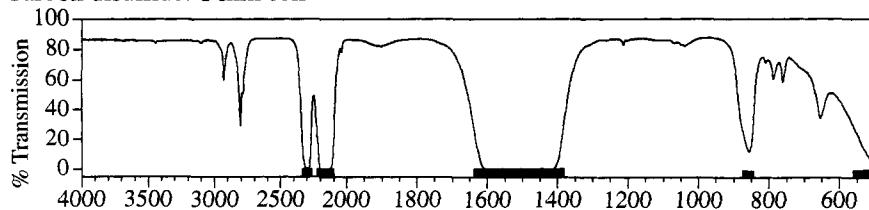


Solvents

Carbon disulfide: 0.2 mm cell



Carbon disulfide: 1 mm cell

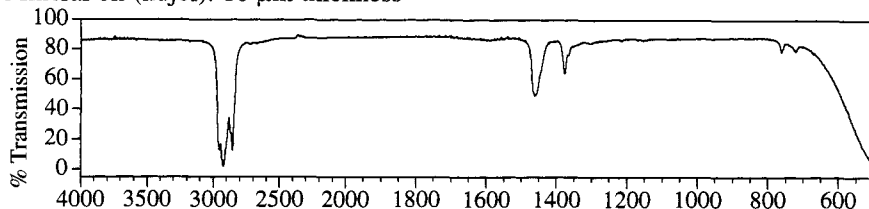


6.14.2

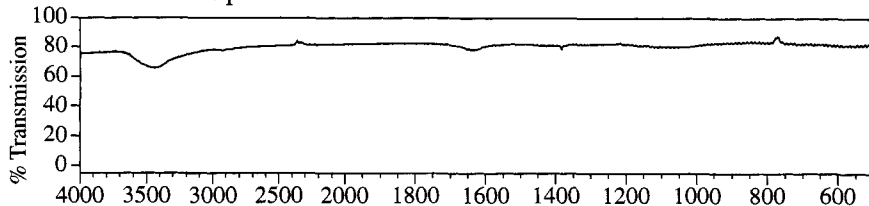
Infrared Spectra of Suspension Media

As it is difficult to prepare pellets and thin mineral oil films of reproducible thickness, the bands of these suspension matrixes are always found superimposed on the sample spectra.

Mineral oil (nujol): 10 μm thickness



Potassium bromide: pellet



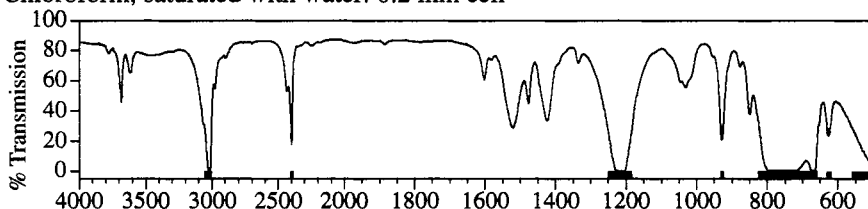
6.14.3

Interferences in Infrared Spectra

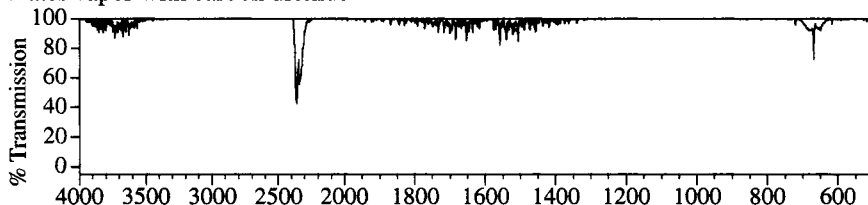
Traces of water in carbon tetrachloride or chloroform may give rise to two bands in the vicinity of 3700 and 3600 cm^{-1} as well as one around 1600 cm^{-1} . At higher concentrations, a broad band at 3450 cm^{-1} is found. Water in the vapor phase exhibits many sharp bands between 2000 and 1280 cm^{-1} . If present in high concentrations, they may temporarily block the detector and appear as shoulders if occurring at a steep side of a strong signal.

Dissolved carbon dioxide shows an absorption band at 2325 cm^{-1} . In solutions that contain amines and traces of water, CO_2 can form carbonates, which lead to the appearance of unexpected bands of protonated N-containing groups. In improperly balanced double beam instruments, gaseous CO_2 can give rise to two signals at approximately 2360 and 2335 cm^{-1} as well as a signal at 667 cm^{-1} .

Chloroform, saturated with water: 0.2 mm cell



Water vapor with carbon dioxide



Commercially available polymers often contain phthalates as plasticizers, which can be found in apparently pure samples and give rise to a band at 1725 cm^{-1} . The presence of such phthalates can be confirmed by MS (m/z 149). In the course of chemical reactions, phthalates may be transformed into phthalic anhydride, which shows a band at 1755 cm^{-1} .

Other frequently encountered contaminants are silicones, which generally exhibit a band at 1625 cm^{-1} , together with a broad signal in the region from 1100 to 1000 cm^{-1} .

7 Mass Spectrometry



7.1

Alkanes [1]

7.1.1

Unbranched Alkanes [2,3]

Fragmentation: Larger alkyl fragments (with $C_{n>4}$) are chiefly formed by direct cleavage. They dehydrogenate and undergo substantial H and skeleton rearrangements. Smaller alkyl fragments (C_2 to C_4) are mainly formed by secondary decomposition of higher alkyl fragments. Eliminations of groups from within the chain (and recombination of its ends) also occur.

Ion series: Consecutive peaks corresponding to C_nH_{2n+1} (m/z 29, 43, 57, 71,...), accompanied by C_nH_{2n-1} (m/z 27, 41, 55, 69,...) and C_nH_{2n} (m/z 28, 42, 56, 70,...) of lower intensity.

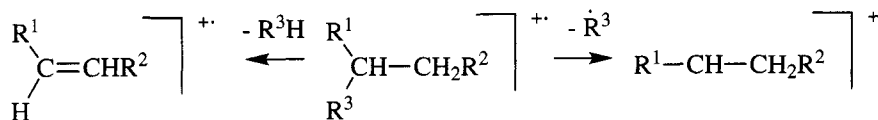
Intensities: Maximum intensity at m/z 43 or 57; with increasing masses, intensity of local maxima smoothly decreasing to a minimum at $[M-15]^+$.

Molecular ion: Medium intensity.

7.1.2

Branched Alkanes

Fragmentation: In most cases, apparently simple bond cleavages, preferably at branched C atoms. The positive charge remains mainly on the branched C atom. Mechanistically, many H and skeleton rearrangements take place. This is reflected by the fact that no specific localization of heavy isotopes is possible.



Ion series: Consecutive peaks corresponding to C_nH_{2n+1} (m/z 29, 43, 57, 71,...), accompanied by C_nH_{2n-1} (m/z 27, 41, 55, 69,...) and C_nH_{2n} (m/z 28, 42, 56, 70,...) of lower intensity.



Intensities: Local intensity maxima at those masses that result from cleavage at branched C atoms if the charge is localized there. Both C_nH_{2n+1} and (often more characteristically) C_nH_{2n} show this tendency.

Molecular ion: Intensity decreasing with increasing degree of branching. No $M^{+\cdot}$ is observed in highly branched systems.

7.1.3

References

- [1] J.T. Bursey, M.M. Bursey, D.G. Kingston, Intramolecular hydrogen transfer in mass spectra. 1. Rearrangements in aliphatic hydrocarbons and aromatic compounds, *Chem. Rev.* **1973**, 73, 191.
- [2] K. Levsen, H. Heimbach, G.J. Shaw, G.W.A. Milne, Isomerization of hydrocarbon ions. VIII. The electron impact induced decomposition of *n*-dodecane, *Org. Mass Spectrom.* **1977**, 12, 663.
- [3] A. Lavanchy, R. Houriet, T. Gäumann, The mass spectrometric fragmentation of *n*-alkanes, *Org. Mass Spectrom.* **1979**, 14, 79.

7.2

Alkenes [1-4]



7.2.1

Unbranched Alkenes

Fragmentation: Dominant loss of alkyl residues and neutral alkenes. The position of highly substituted double bonds can be localized because in this case alkene eliminations are specific McLafferty-type reactions. Otherwise, double bonds can be localized in derivatives, such as epoxides and glycols, or by means of low energy ionization techniques. Branching effects are less characteristic than in isoalkanes. Alicyclic compounds exhibit very similar spectra.

Ion series: Consecutive peaks corresponding to $\text{C}_n\text{H}_{2n-1}$ (m/z 41, 55, 69, 83,...), accompanied by alkyl and alkene ions, $\text{C}_n\text{H}_{2n+1}$ (m/z 43, 57, 71, 85,...) and C_nH_{2n} (m/z 42, 56, 70, 84,...), mostly of lower intensity.

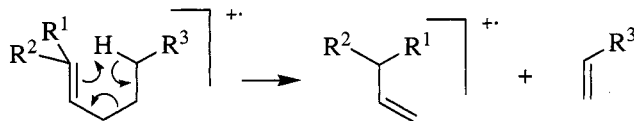
Intensities: Dominant maxima in the lower mass range, peaking around C_4 . Local even-mass maxima due to alkene eliminations if the double bond is highly substituted.

Molecular ion: Significant, but not necessarily strong.

7.2.2

Branched Alkenes

Fragmentation: Highly substituted double bonds are less easily displaced than the unsubstituted ones and give rise to specific alkene eliminations of the McLafferty type, resulting in significant local maxima corresponding to C_nH_{2n} (cf. scheme). The latter may allow to localize the double bond. With unsubstituted double bonds, no reliable localization is possible and only moderately useful branching effects can be observed. The branching position is more easily determined after reduction to an alkane (in situ in GC/MS with H_2 as carrier gas and heated Pt wool as catalyst).



Ion series: Maxima of the alkene type ($\text{C}_n\text{H}_{2n-1}$; m/z 41, 55, 69, 83,...), accompanied by weaker alkyl fragments, $\text{C}_n\text{H}_{2n+1}$ (m/z 43, 57, 71, 85,...), in the low mass range and more significant alkene ions, C_nH_{2n} (m/z 42, 56, 70, 84,...).

Intensities: Intensive peaks in the lower mass range. Diagnostically important local maxima of even mass, frequently also in the higher mass range.

Molecular ion: Usually significant.

7.2.3

Polyenes and Polyynes

Fragmentation: The spectra of aliphatic compounds with several triple and/or double bonds are similar to those of aromatic hydrocarbons.

Ion series: Very similar to those of aromatic hydrocarbons, but fragments with higher hydrogen contents than in aromatics (m/z 54, 55; 66, 67; 79, 80) are usually found in polyenes and polyynes.

Intensities: Very similar distribution of peak intensities as for aromatic hydrocarbons.

Molecular ion: Usually strong, as in aromatic hydrocarbons.

7.2.4

References

- [1] A.G. Loudon, A. Maccoll, The mass spectrometry of the double bond. In: *The Chemistry of Alkenes*; J. Zabicky, Ed.; Interscience: London, 1970; p 327.
- [2] J.T. Bursey, M.M. Bursey, D.G. Kingston, Intramolecular hydrogen transfer in mass spectra. 1. Rearrangements in aliphatic hydrocarbons and aromatic compounds, *Chem. Rev.* **1973**, 73, 191.
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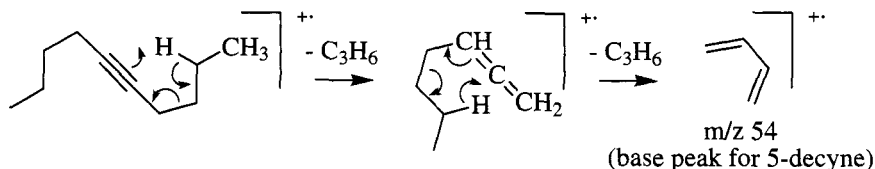
7.3

Alkynes [1]

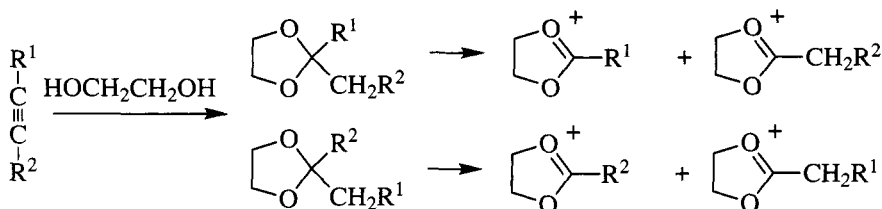
7.3.1

Aliphatic Alkynes

Fragmentation: Tendency to lose a non-acetylenic H[•] from M^{•+}. Extensive rearrangements (including consecutive McLafferty rearrangements to the triple bond) result in uncharacteristic degradation:



Rearrangement products at m/z 82 and 96 are dominant in nonbranched alkynes with $C_{n>8}$. Consecutive loss of methyl radical occurs. In general, no reliable localization of the triple bond is possible except in derivatives (as in ethylene glycol adducts [1], see scheme).



Ion series: Prominent peaks for C_nH_{2n-3} (m/z 25, 39, 53, 67, 81,...), accompanied by C_nH_{2n-1} (m/z 41, 55, 69, 83,...) and alkyl ions C_nH_{2n+1} (m/z 43, 57, 71, 85,...). Occasionally even-mass maxima for C_nH_{2n-2} (m/z 26, 40, 54, 68, 82,...).

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Weak or missing in spectra of smaller molecules, significant in those of larger ones. Generally, $[M-1]^+$ is present. In terminal alkynes, it is normally more abundant than $M^{•+}$.

7.3.2

References

- [1] C. Lifshitz, A. Mandelbaum, Mass spectrometry of acetylenes. In: *The Chemistry of the Carbon-Carbon Triple Bond*; S. Patai, Ed.; Wiley: New York, 1978; p 157.

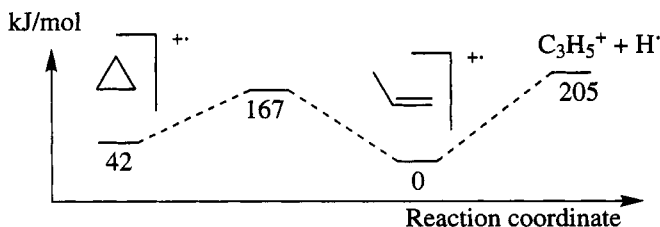
7.4

Alicyclic Hydrocarbons [1]

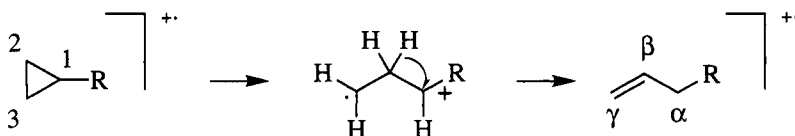
7.4.1

Cyclopropanes [2,3]

Fragmentation: Generally, spectra of cyclopropanes and alkenes are very similar because at 70 eV ionization, the ring readily isomerizes to corresponding alkene radical cations.



Preferred primary fragmentation by bond cleavage at branched C atoms. Loss of alkyl residues and of neutral alkenes dominates. The ring of monosubstituted cyclopropanes is opened exclusively at the 1,2- and not the 2,3- bond. The primarily formed double bond is predominantly (for R: OCH₃) or exclusively (for R: H, alk, COOCH₃) found in the β,γ -position (even for COOCH₃, where the α,β -unsaturation is thermodynamically more stable).



Molecular ions of cyclopropyl cyanide, allyl cyanide, methacrylonitrile, and pyrrole rearrange to one common radical ion, most likely that of pyrrole [4].

Ion series: Consecutive maxima corresponding to C_nH_{2n-1} (m/z 41, 55, 69, 83,...), accompanied by alkyl and alkenyl ions of the type C_nH_{2n+1} (m/z 43, 57, 71, 85,...) and C_nH_{2n} (m/z 42, 56, 70, 84,...), mostly of lower intensity.

Intensities: Dominant peaks in the low mass range, peaking around C_4 . Local even-mass maxima due to alkene eliminations if the resulting double bond is highly substituted.

Molecular ion: Significant, but not necessarily strong.

7.4.2

Saturated Monocyclic Alicyclics [5]

Fragmentation: Preferred primary fragmentation by bond cleavage at branched C atoms, followed by loss of alkyl residues and alkenes.

Ion series: Consecutive maxima corresponding to C_nH_{2n-1} (m/z 41, 55, 69, 83,...), accompanied by C_nH_{2n+1} (m/z 43, 57, 71, 85,...) and C_nH_{2n} (m/z 42, 56, 70, 84,...) of lower intensities. In general, the maxima are so similar to those of alkenes that no clear distinction is possible.

Intensities: Overall distribution of peaks maximizing in the lower mass range, around C_4 or C_5 . Local maxima can result from branching effects.

Molecular ion: Significant, mostly of medium intensity.



7.4.3

Polycyclic Alicyclics

Fragmentation: Most important primary cleavage at highly branched carbon atoms, followed by H rearrangements and complex fragmentations.

Ion series: With increasing number of rings, the position of unsaturated hydrocarbon fragments in the upper m/z range shifts from C_nH_{2n-1} (m/z 41, 55, 69, 83,...) to C_nH_{2n-3} (m/z 39, 53, 67, 81,...) and to C_nH_{2n-5} (m/z 51, 65, 79, 93,...). Typically, maxima in the lower m/z range have a lower degree of unsaturation than those in the upper m/z range.

Intensities: Major maxima evenly distributed, somewhat more intense in the high mass or M^{++} range.

Molecular ion: Strong.

7.4.4

Cyclohexenes

Fragmentation: Loss of larger ring substituents as well as retro-Diels–Alder reaction, yielding even-mass maxima with one or two double-bond equivalents, C_nH_{2n} (m/z 42, 56, 70, 84,...) and C_nH_{2n-2} (m/z 40, 54, 68, 82,...), unless the retro-Diels–Alder product corresponds to ethylene. Somewhat unexpectedly, the base peak of cyclohexene is at $[M-15]^+$.

The retro-Diels–Alder reaction often accounts for prominent fragments of cyclohexenes and 1,4-cyclohexadienes:



However, double-bond migration may or may not occur beforehand. Also, other fragmentation pathways may dominate. Therefore, a reliable localization of the

double bond in cyclohexene derivatives of unknown structure is not necessarily possible. For example, the base peak of 1,2-dimethylcyclohexene is at m/z 68 rather than at the expected m/z 82.

Ion series: Unsaturated hydrocarbon fragments in the upper m/z range are shifted, relative to cyclohexane fragments, by two mass units to C_nH_{2n-3} (m/z 39, 53, 67, 81,...). Typically, maxima in the lower m/z range have a lower degree of unsaturation than those in the upper m/z range.

Intensities: Intensive peaks evenly distributed over whole mass range.

Molecular ion: Medium intensity (ca. 40% in cyclohexene).



7.4.5 References

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- [2] H. Schwarz, The chemistry of ionized cyclopropanes in the gas phase. In: *The Chemistry of the Cyclopropyl Group*; Z. Rappoport, Ed.; Wiley: Chichester, 1987; p 173.
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- [5] E.F.H. Brittain, C.H.J. Wells, H.M. Paisley, Mass spectra of cyclobutanes and cyclohexanes of molecular formula $C_{10}H_{16}$, *J. Chem. Soc. B* **1968**, 304.

7.5

Aromatic Hydrocarbons [1-4]

7.5.1

Aromatic Hydrocarbons

Fragmentation: Weak tendency of fragmentation. Elimination of H^+ and successive H_2 eliminations, yielding $[M-1]^+$, $[M-3]^+$, and $[M-5]^+$ of decreasing intensities. In condensed aromatics, $[M-2]^+$ can be a dominating fragment. Further typical fragmentation reactions are the eliminations of acetylene (Δm 26) and C_3H_3 (Δm 39). Some CH_3 elimination frequently occurs in pure aromatic compounds. In the case of diphenyl compounds, biphenylene (m/z 152) and, if a CH_2 group is available, fluorene (m/z 165) ions are typically observed.

Ion series: C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...), for polycyclic aromatics gradually changing to more highly unsaturated ions. Doubly charged ions frequently occur, increasingly with increasing number of π -electron systems.

Intensities: Weak fragments. The intensity pattern of doubly charged ions does not follow that of the corresponding singly charged ions.

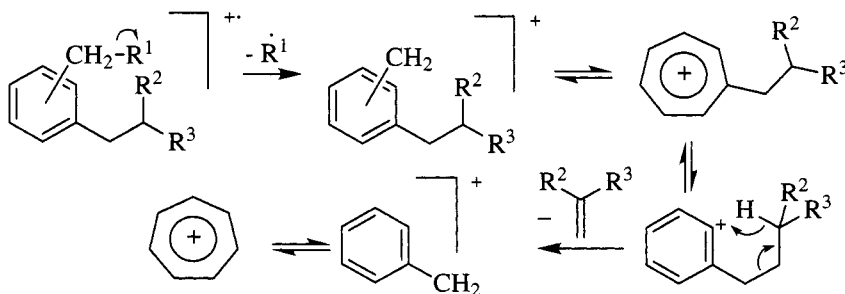
Molecular ion: Strong.



7.5.2

Alkylsubstituted Aromatic Hydrocarbons

Fragmentation: Dominant loss of alkyl residues by benzylic cleavage, followed by elimination of alkenes.



At low resolution, ethylbenzyl and β -phenylethyl are isobaric with benzoyl (m/z 105). In contrast to benzoyl, dehydrogenation products (m/z 104, 103) as well as protonated benzene (m/z 79) are also present if m/z 105 is a hydrocarbon rest.

Ion series: Aromatic hydrocarbon fragments, C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...), in the lower mass range.

Intensities: Intensive peaks mainly in the higher mass range. Maxima by benzylic cleavage.

Molecular ion: Strong or medium.

7.5.3**References**

- [1] J.T. Bursey, M.M. Bursey, D.G. Kingston, Intramolecular hydrogen transfer in mass spectra. 1. Rearrangements in aliphatic hydrocarbons and aromatic compounds, *Chem. Rev.* **1973**, 73, 191.
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7.6 Heteroaromatic Compounds [1,2]

7.6.1 General Characteristics

Fragmentation: Mostly fragments of aromatic character with specific eliminations including heteroatoms, e.g., elimination of HCN, CO, CHO, CS, and CHS from $M^{+\cdot}$ and of HCN, CO, and CS from fragments. In the case of alkylsubstituted heteroaromatics, occurrence of benzylic-type cleavage and McLafferty rearrangements of substituents with $C_{n>1}$, as well as specific rearrangements including heteroatoms, especially in N aromatics.

Ion series: Aromatic hydrocarbon fragments C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65,...) in the lower mass range if the necessary number of C atoms is present (no such fragments, e.g., in pyrazine). Ions including heteroatoms like $HCN^{+\cdot}$ (m/z 27), CH_3CNH^+ (m/z 42), and $CS^{+\cdot}$ (m/z 44).

Intensities: Intensive peaks mainly in the higher mass range.

Molecular ion: Generally strong. $[M-1]^+$ is often relevant in alkylsubstituted heteroaromatics.



7.6.2 Furans [3]

Fragmentation: Oxygen can be lost from $M^{+\cdot}$ together with the neighboring C as CHO (Δm 29). In 2- or 6-methyl-furans, CH_3CO^+ (m/z 43) can be seen (base peak in 2,5-dimethylfuran). As in aromatic methyl ethers, $[M-43]^+$ is a product of a two-step reaction: $(M^{+\cdot}-CH_3^{\cdot}-CO)$. Furans substituted with an alkyl group ($C_{n>1}$): benzylic-type cleavage (to pyrylium ion $C_5H_5O^+$, m/z 81), followed by loss of CO.

Ion series: Mainly aromatic hydrocarbon fragments C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65,...).

Intensities: Intensive peaks mainly in the higher mass range. The fragments are usually stronger than in purely aromatic hydrocarbons.

Molecular ion: Strong. No pronounced tendency to protonate. Usually, $[M-1]^+$ is very strong in methylfurans.

7.6.3 Thiophenes [4]

Fragmentation: Sulfur can be lost from $M^{+\cdot}$ together with the neighboring C as CHS (Δm 45) or CS (Δm 44). Typical for thiophenes substituted with an alkyl group ($C_{n>1}$) is benzylic-type cleavage followed by loss of CS (Δm 44). Protonated thiophene (m/z 85) is a characteristic product of monoalkylated thiophenes.

Ion series: Aromatic hydrocarbon fragments C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65,...). Besides the isotope peak ($M+2$), the signals at m/z 44 and 45 (CS^+ and CHS^+) are indicators for sulfur.

Intensities: Dominant peaks for M^+ and products of benzylic-type cleavage.

Molecular ion: Strong. Characteristic S isotope signal ($[M+2]^+$ corresponds to 4.4% of M^+). No pronounced tendency of protonation. Usually, $[M-1]^+$ is very strong in methylthiophenes.

7.6.4

Pyrroles [5]

Fragmentation: HCN elimination from M^+ and from fragments. In methylpyrroles, $[M-1]^+$ is dominant. Benzylic-type cleavage in C- and N-alkylpyrroles with or without (non-specific) H rearrangements.

Ion series: Aromatic hydrocarbon fragments C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65,...).

Intensities: Dominant peaks for M^+ and products of benzylic-type cleavage.

Molecular ion: Strong (odd mass for odd number of N in the molecule). No tendency to protonate. In methylsubstituted pyrroles, $[M-1]^+$ is dominant.

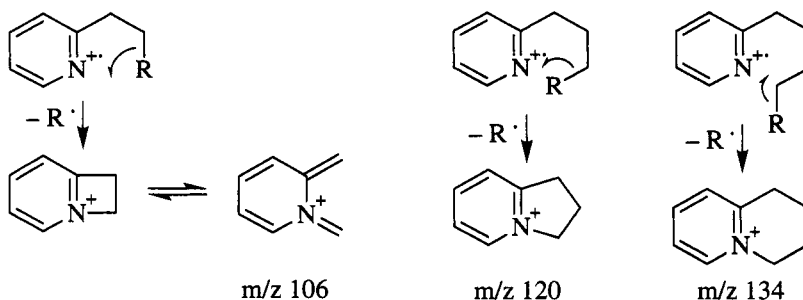


7.6.5

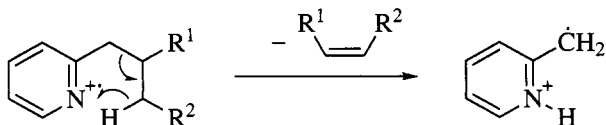
Pyridines

Fragmentation: HCN elimination (Δm 27) from fragments and the ion H_2CN^+ (m/z 28) are characteristic. Additional reactions in 2- or 6-methylpyridines are CH_3CN elimination (Δm 41) and the formation of CH_3CNH^+ (m/z 42). Benzylic cleavage is dominant for 3-alkyl-, strong for 4-alkyl-, and weak for 2-alkylpyridines. Typical rearrangements with participation of the N atom in 2- and 6-alkylpyridine derivatives.

Intramolecular N-alkylation in 2-alkyl derivatives:



McLafferty rearrangements are important in 2- and 4-alkylpyridines:



Ion series: Aromatic hydrocarbon fragments, C_nH_n , $C_nH_{n\pm 1}$ and $C_nH_{n\pm 1}N$ (m/z 39–41, 51–54, 63–67, 75–80,...).

Intensities: Dominant peaks for $M^{+\cdot}$ or, if possible, for products of benzylic-type cleavage.

Molecular ion: Strong except when benzylic-type cleavage is possible. Odd mass for an odd number of N in the molecule. No tendency to protonate. $[M-1]^+$ is usually present and is strong in alkylsubstituted pyridines.

7.6.6

N-Oxides of Pyridines and Quinolines



Fragmentation: The $[M-O]^{+\cdot}$ ion, with variable intensity, is probably due to thermal decomposition. The fragments $[M-CO]^{+\cdot}$ and, if an alkyl group is present on the neighboring C atom, $[M-OH]^{+\cdot}$ are relevant for quinoline *N*-oxides. Rearrangements with ring formation including the N–O moiety if alkyl or aryl groups are present in the neighboring positions.

Ion series: As for the corresponding heteroaromatics, too, aromatic hydrocarbon fragments C_nH_n , $C_nH_{n\pm 1}$ and $C_nH_{n\pm 1}N$ (m/z 39–41, 51–54, 63–67, 75–80,...) are observed.

Intensities: Dominant peaks for $M^{+\cdot}$ and products of benzylic-type cleavage.

Molecular ion: Strong, except when $[M-O]^{+\cdot}$ dominates due to experimental conditions or when benzylic-type cleavage is possible. Odd mass for odd number of N atoms in the molecule. No tendency to protonate.

7.6.7

Pyridazines and Pyrimidines

Fragmentation: Loss of N_2 and CH_2N^{\cdot} from pyridazines to yield $M-28$. Also, loss of N_2H^{\cdot} (especially important in methylpyridazines) to give $[M-29]^+$. In pyridazine *N*-oxides, consecutive loss of NO^{\cdot} and HCN . Consecutive loss of two HCN (Δm 27) molecules from pyrimidines. In 2-, 4-, and 6-methylpyrimidines, CH_3CN is eliminated (Δm 41) and the ion $CH_3CNH^{+\cdot}$ (m/z 42) occurs.

Ion series: Aromatic hydrocarbon fragments (C_nH_n , $C_nH_{n\pm 1}$) and, for pyrimidines, $C_nH_{n\pm 1}N$, at low masses (m/z 39, 51–53).

Intensities: Dominant peak for $M^{+\cdot}$.

Molecular ion: Strong. No tendency to protonate. For pyrimidines, $[M-1]^+$ is usually observable.

7.6.8

Pyrazines

Fragmentation: Consecutive losses of two HCN (Δm 27) molecules. For methylpyrazines, elimination of CH_3CN (Δm 41) and formation of CH_3CNH^+ (m/z 42).

Ion series: No aromatic character of the spectra.

Intensities: Dominant peak for $\text{M}^{+\cdot}$.

Molecular ion: Strong. No tendency to protonate. Usually, $[\text{M}-1]^+$ is observable; it can be stronger than $\text{M}^{+\cdot}$ in alkylsubstituted ($\text{C}_{n>1}$) pyrazines.

7.6.9

Indoles



Fragmentation: Analogous to pyrrole; HCN elimination (Δm 27) from $\text{M}^{+\cdot}$ and from fragments. From $\text{M}^{+\cdot}$ also $\text{H}_2\text{CN}^{\cdot}$ (Δm 28) elimination (in one or two steps). In methylsubstituted indoles, $[\text{M}-1]^+$ is dominant. In *N*-methylindoles, $[\text{M}-15]^+$ is significant. Benzylic-type cleavage in *C*- and *N*-alkylindoles with or without (non-specific) H rearrangements.

Ion series: Aromatic ion series.

Intensities: Dominant maxima in the higher mass range.

Molecular ion: Strong. No tendency to protonate. In methylsubstituted indoles, $[\text{M}-1]^+$ is strong.

7.6.10

Quinolines and Isoquinolines

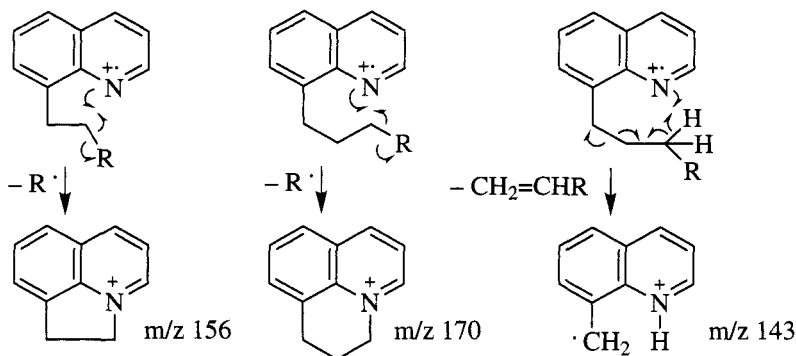
Fragmentation: Similar to pyridine: HCN elimination (Δm 27) from $\text{M}^{+\cdot}$, $[\text{M}-1]^+$, and fragments. In methylquinolines and isoquinolines also CH_3CN eliminations (Δm 41). In alkylsubstituted ($\text{C}_{n>1}$) quinolines, benzylic cleavage dominates except when neighboring effects of N can play a role. For 2- and 8-alkylquinolines, as well as 1- and 3-alkylisoquinolines, see rearrangements in pyridines.

Ion series: Aromatic hydrocarbon fragments, C_nH_n , $\text{C}_n\text{H}_{n\pm 1}$, and $\text{C}_n\text{H}_{n\pm 1}\text{N}$ (m/z 39–41, 51–54, 63–67, 75–80,...).

Intensities: Dominant peak for $\text{M}^{+\cdot}$ or, if possible, for products of benzylic-type cleavage.

Molecular ion: Strong, except when benzylic-type cleavage is possible. Odd mass for odd number of N atoms in the molecule. No tendency to protonate. $[\text{M}-1]^+$ is usually present and is strong in alkylsubstituted quinolines.

Rearrangements in 8-alkylquinolines:



7.6.11

Cinnoline, Phthalazine, Quinazoline, Quinoxaline



Fragmentation: Same as for the corresponding monocyclic heteroaromatics pyridazine, pyrimidine, and pyrazine. Characteristic for pyridazine, cinnoline, and phthalazine is the elimination of N_2 (Δm 28) and of N_2H^+ (Δm 29) from their alkyl derivatives. Phthalazine loses HCN (Δm 27) twice.

Ion series: Aromatic hydrocarbon fragments (C_nH_n , $C_nH_{n\pm 1}$) and $C_nH_{n\pm 1}N$ (m/z 39–41, 51–54, 63–67, 75–80,...).

Intensities: Dominant maximum for $M^{+\cdot}$ or, if possible, for products of benzylic-type cleavage.

Molecular ion: Strong, except when benzylic-type cleavage is possible. Odd mass for odd number of N atoms in the molecule. No tendency to protonate. $[M-1]^+$ is usually present and is strong in alkylsubstituted compounds.

7.6.12

References

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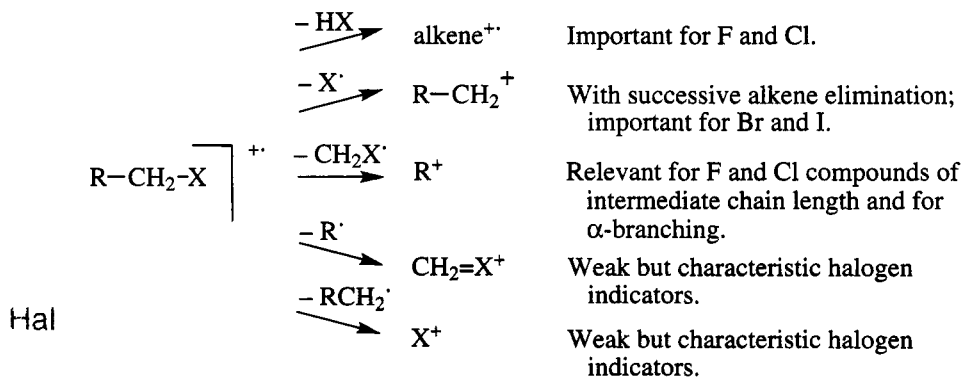
7.7

Halogen Compounds [1-3]

7.7.1

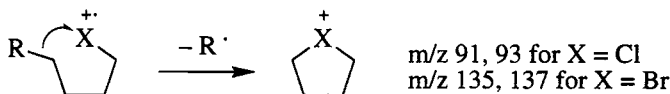
Saturated Aliphatic Halides

Fragmentation: Loss of halogen radical ($I > Br > Cl > F$) followed by elimination of alkenes. Loss of alkyl radical followed by elimination of acid HX. Loss of acid HX to give an alkene radical cation.



Ion series: The dominant hydrocarbon fragments are mainly alkenyl fragments ($\text{C}_n\text{H}_{2n-1}$) for F and Cl, mixed alkyl ($\text{C}_n\text{H}_{2n+1}$) and alkenyl fragments ($\text{C}_n\text{H}_{2n-1}$) for Br, and mainly alkyl fragments ($\text{C}_n\text{H}_{2n+1}$) for I.

Intensities: Intensive peaks mainly in the lower mass range. Characteristic maxima for Cl and Br at $\text{C}_4\text{H}_8\text{X}$ (m/z 91/93 and 135/137, respectively), which has a cyclic structure:



Alkyl substituents on the chain reduce the intensity of this fragment. If it is strong, $[\text{M}-\text{X}]^+$ is weak. In the case of iodoalkanes some I^+ and $\text{HI}^{\bullet+}$ at m/z 127, 128 is usually detectable.

Molecular ion: Strong for the smallest alkanes, with increasing intensity in the sequence F, Cl, Br, I. Decreases rapidly with increasing mass and with increasing branching. It is negligible for F and Cl if the n -alkyl chains are longer than pentyl, and for Br and I if they are longer than heptyl and nonyl, respectively. Low tendency to protonate. Characteristic isotope patterns for Cl and Br. Iodine can be detected because of its high mass; the ^{13}C signals of $\text{M}^{\bullet+}$ and its fragments are conspicuously weak.

7.7.2

Polyhaloalkanes

Fragmentation: Preferred fragmentation of the C–C bond if several halogen atoms are bonded to one of these carbon atoms. CF_3 (m/z 69) is often the base peak in terminally perfluorated alkanes, and so is CHCl_2 (m/z 83, 85, 87) in terminally dichlorinated compounds. Often, X_2 is eliminated besides the usual fragmentation of X^\cdot and HX . Interchange of halogens may occur. For example, m/z 85 (CF_2Cl) is a dominant signal (ca. 60%) for CF_3CFCI_2 .

Ion series: Most fragments are halogenated alkyl and alkenyl groups, easily detectable on the basis of the isotope signals in the cases of Cl and Br.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Weak, decreasing with increasing number of halogen atoms. Absent from the spectra of many polyhalogenated compounds.

7.7.3

Aromatic Halides

Fragmentation: Consecutive losses of halogen radicals and/or acid HX . In perhalogenated aromatics, decomposition down to C_x^+ , with x from 1 to 6 (m/z 12, 24, 36, 48, 60, 72). If alkylsubstituted ($\text{C}_{n>1}$), the base peak is mostly the result of benzylic cleavage. In an otherwise aromatic environment, m/z 57 is a F indicator ($\text{C}_3\text{H}_2\text{F}^+$). Elimination of CF_2 (Δm 50) from CF_3 groups attached to the aromatic ring (from $\text{M}^{+\cdot}$ or from fragments).

Ion series: Aromatic hydrocarbon fragments, C_nH_n , C_nH_{n-1} , and C_nH_{n-2} (m/z 39, 51–53, 63–65, 75–77,...). In the higher mass range: $\text{C}_n(\text{H,X})_n$.

Intensities: Dominant peaks in the $\text{M}^{+\cdot}$ region.

Molecular ion: Usually very strong. Characteristic isotope signals for Cl and Br.

7.7.4

References

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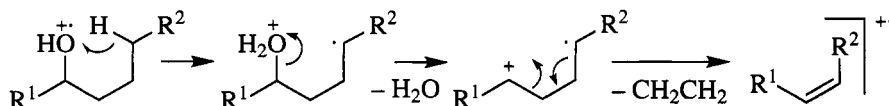
7.8

Alcohols, Ethers, and Related Compounds [1,2]

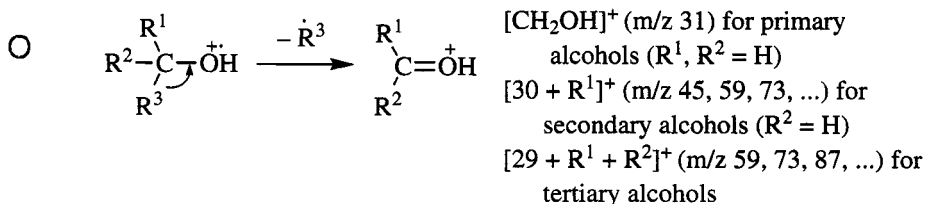
7.8.1

Aliphatic Alcohols [3]

Fragmentation: Elimination of water from $M^{+\cdot}$ and from fragments. Strong for primary alcohols. If an aliphatic H atom can be transferred in a 6-ring process, it is involved in the water elimination in 90% of the investigated cases. If a CH_2CH_2 group is attached to the O-bearing C atom, water elimination is often followed by loss of ethylene. Water elimination is dominant for long-chain alcohols, making their spectra similar to those of alkenes.



Cleavage of bonds next to the OH-bearing C atom to form oxonium ions, then elimination of water and of alkenes. The α -cleavage is often dominant. Usually, its importance increases with increasing branching at the α -carbon atom. The larger substituent is lost most readily.



Consecutive H_2O and alkene eliminations in longer chain primary alcohols lead to $[\text{M}-46]^+$, $[\text{M}-74]^+$, $[\text{M}-102]^+$, The series of fragments at $[\text{M}-15]^+$, $[\text{M}-18]^+$, and $[\text{M}-33]^+$ is frequently observed for branched alcohols.

Ion series: Dominant consecutive alkene ions corresponding to $\text{C}_n\text{H}_{2n-1}$ ($m/z\ 41, 55, 69, \dots$), C_nH_{2n} ($m/z\ 42, 56, 70, \dots$), accompanied by weaker fragments, $\text{C}_n\text{H}_{2n+1}\text{O}$ ($m/z\ 31, 45, 59, \dots$), with one or more local maxima in the latter series ($m/z\ 31$ dominates in primary alcohols).

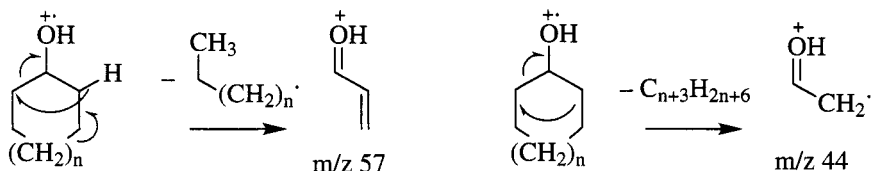
Intensities: Major peaks in the lower mass range from alkyl- and alkene-type ions with weaker maxima from ions of the sort $\text{C}_n\text{H}_{2n+1}\text{O}$.

Molecular ion: Mostly weak, often missing, especially in tertiary and long-chain alcohols. Indirect determination of $M^{+\cdot}$ is often possible from the fragments at $[\text{M}-15]^+$, $[\text{M}-18]^+$ and $[\text{M}-33]^+$. $[\text{M}+1]^+$ is often significant. In primary and secondary alcohols also $[\text{M}-1]^+$ can usually be seen. Sometimes, $[\text{M}-2]^+$ is formed because of oxidation to carbonyl compounds during sample introduction.

7.8.2

Alicyclic Alcohols [3]

Fragmentation: Elimination of water from $M^{+\cdot}$, followed by loss of alkyl or alkenyl residues. Ring cleavage at the O-bearing C atom, followed by loss of alkyl residues after H rearrangement.



Ion series: Alkene hydrocarbon fragments $\text{C}_n\text{H}_{2n-1}$ (m/z 41, 55, 69,...), $\text{C}_n\text{H}_{2n-3}$ (m/z 39, 53, 67, 81,...), and unsaturated O fragments, $\text{C}_n\text{H}_{2n-1}\text{O}$ (m/z 43, 57, 71,...), as well as acetaldehyde and its homologues (m/z 44, 58, 72,...).

Intensities: Local maxima evenly distributed over whole mass range.

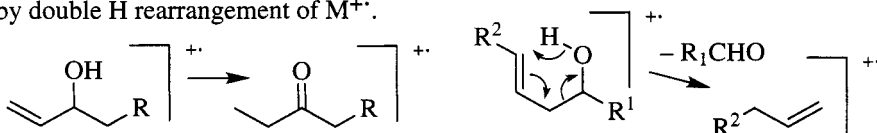
Molecular ion: Usually weak but in contrast to aliphatic alcohols practically never missing. $[M+1]^+$ usually contains a significant amount of protonated molecule ion.

7.8.3

Unsaturated Aliphatic Alcohols [3]

Allyl alcohols: The spectra are similar to those of the corresponding carbonyl compounds, which are (partly) formed by double H rearrangement of $M^{+\cdot}$.

γ,δ -Unsaturated alcohols: Aldehyde elimination through a McLafferty-type rearrangement:



7.8.4

Vicinal Glycols

Fragmentation: Cleavage of bonds next to the OH-bearing C atom (α -cleavage) dominates. Preferable fragmentation of the C–C bond between the two oxygens, the charge remaining mainly on the larger fragment. Water elimination from these fragments, but scarcely from $M^{+\cdot}$.

Ion series: Saturated and unsaturated aliphatic ions (m/z 43, 57, 71,... and 41, 55, 69,...) and intense peaks from O-containing saturated rests (m/z 45, 59, 73,...).

Intensities: Dominant peaks for the products of α -cleavages and their dehydrated derivatives.

Molecular ion: Weak.

7.8.5

Aliphatic Hydroperoxides [4]

Fragmentation: Most pronounced is the loss of the hydroperoxy radical HO_2^\cdot (Δm 33), especially when a tertiary alkyl cation is formed. Important, in decreasing order, is loss of H_2O_2 (Δm 34), H_2O (Δm 18), HO^\cdot (Δm 17), and O (Δm 16).

Ion series: Mainly saturated and unsaturated alkyl fragments, $\text{C}_n\text{H}_{2n+1}$ (m/z 43, 57, 71,...) and $\text{C}_n\text{H}_{2n-1}$ (m/z 41, 55, 69,...). The oxygen-indicating fragments at m/z 31 and its homologues are always present.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Weak.

7.8.6

Phenols

Fragmentation: Decarbonylation (Δm 28) and loss of CHO^\cdot (Δm 29) followed by elimination of acetylene. In alkyl derivatives $[\text{M}-1]^+$ and, if at least two alkyl carbons are present (dimethyl or ethyl), $[\text{M}-15]^+$ become important. Elimination of CO from the primary fragments. $[\text{M}-18]^{++}$ mainly with *ortho*-alkylphenols. In derivatives with a longer alkyl chain, benzylic cleavage and alkene elimination (McLafferty rearrangement) are the dominant primary fragmentation processes. The fragments then lose CO (Δm 28).

Ion series: Aromatic hydrocarbon fragments C_nH_n and C_nH_{n+1} (m/z 39, 51–53, 63–65, 75–77,...). The presence of some m/z 55 ($\text{C}_3\text{H}_3\text{O}$) is common. A peak at m/z 69 ($\text{O}\equiv\text{CCH}=\text{C}=\text{O}$) is characteristic of 1,3-dihydroxy substitution.

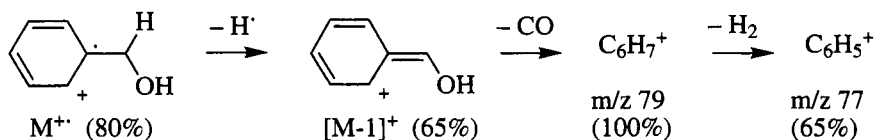
Intensities: Dominant peaks in the higher mass range.

Molecular ion: Dominant, no tendency to form $[\text{M}+\text{H}]^+$. $[\text{M}-1]^+$ is weak.

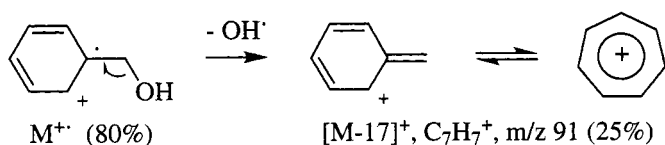
7.8.7

Benzyl Alcohols

Fragmentation: Loss of H^\cdot and consecutive elimination of CO (Δm 28) to give a protonated benzene molecule, which further loses H_2 .



Elimination of OH^\cdot (Δm 17) to yield the tropylium cation is the second important fragmentation path:



Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

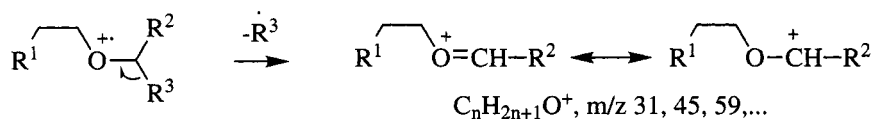
Intensities: Dominant peaks for the products described under Fragmentation. For benzyl alcohol decreasing in the sequence of $[\text{M}-29]^+$, M^+ , $[\text{M}-1]^+$, $[\text{M}-31]^+$, $[\text{M}-17]^+$.

Molecular ion: Strong.

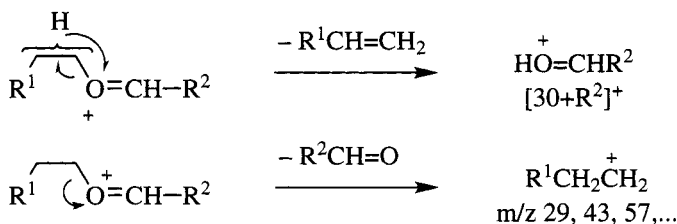
7.8.8

Aliphatic Ethers [5,6]

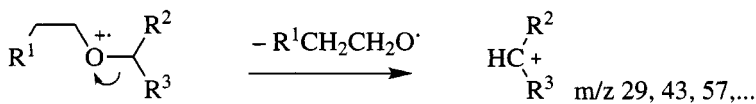
Fragmentation: Homolysis of the C–C bond next to the O atom to yield oxygen-containing fragments. Preferably, the bond at the highest substituted C atom breaks and the larger alkyl group is lost.



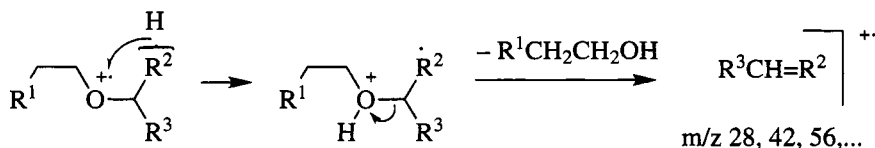
This homolysis is followed by the elimination of alkenes, carbonyls, or, less importantly, of water.



As a competing process, especially with increasing molecular weight, heterolysis at the O atom takes place to yield strong alkyl ion signals. The larger as well as the branched alkyl rests are fragmented preferably. The base peak often arises from heterolysis of the C–O bond.



In contrast to the H_2O elimination from alcohols, the H transfer involved in the elimination of $\text{RCH}_2\text{CH}_2\text{OH}$ from ethers is non-specific.



Ion series: Alkyl fragments, $\text{C}_n\text{H}_{2n+1}$ (m/z 29, 43, 57,...), with maxima due to cleavage of the C–O bond. Alkene ion series, C_nH_{2n} (m/z 28, 42, 56,...), due to elimination of alcohol. Oxygen-containing fragments $\text{C}_n\text{H}_{2n+1}\text{O}$ (m/z 31, 45, 59,...) with maxima due to cleavage of the C–C bond next to oxygen.

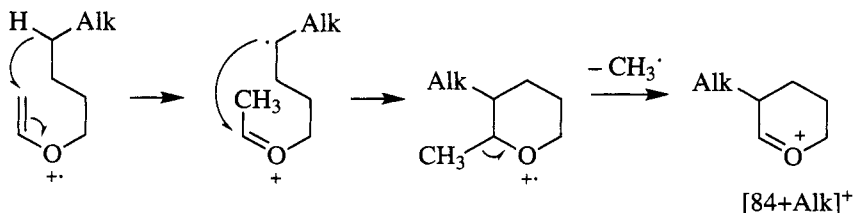
Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Significant or weak. Decreasing with increasing chain length and branching.

7.8.9

Unsaturated Ethers [7]

Fragmentation of vinylic and acetylenic alkyl ethers: Dominant homolysis of the alkyl C–C bond next to the O atom on the saturated side, leading to $\text{C}_3\text{H}_5\text{O}^+$ (m/z 57) for vinylic and $\text{C}_3\text{H}_3\text{O}^+$ (m/z 55) for acetylenic ethers of primary aliphatic alcohols. For alkyl ($\text{C}_{n>5}$) vinyl ethers, ethanol elimination after triple H transfer. $[\text{M}-15]^+$ in vinyl ethers predominantly by elimination of the vinyl CH_2 after H rearrangement.



Fragmentation of allylic ethers: Heterolysis of both C–O bonds, leading to strong C_3H_5^+ (m/z 41) and alkyl (m/z 29, 43, 57,...) cations. Formation of ionized allylic alcohol (m/z 58) by non-specific H transfer from the alkyl rest. In allylic and propargylic ethers, no cleavage of the C–C bond next to the O atom of the alkenyl group occurs. Hence, loss of vinyl or acetylenyl cannot be observed.

Ion series: $\text{C}_n\text{H}_{2n}\text{O}$ (m/z 44, 58, 72,...) for alkenyl alkyl ethers and $\text{C}_n\text{H}_{2n-2}\text{O}$ (m/z 42, 56, 70,...) for dialkenyl ethers. Unsaturated aliphatic ($\text{C}_n\text{H}_{2n-1}$; m/z 41, 55, 69,...) as well as saturated aliphatic and unsaturated oxygen-containing fragments ($\text{C}_n\text{H}_{2n+1}$ and $\text{C}_n\text{H}_{2n-1}\text{O}$; m/z 43, 57, 71,...).

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Weak to medium, very weak for acetylenic ethers.

7.8.10

Alkyl Cycloalkyl Ethers

Fragmentation of methyl ethers of cycloalkanols with > 3 C atoms: After primary cleavage of the ring C–C bond next to the O atom, the prominent fragments formed are $\text{CH}_3\text{OCH}=\text{CH}_2^{+\cdot}$ (m/z 58) and, for alicyclics with > 4 C atoms, $\text{CH}_3\text{O}=\text{CHCH}=\text{CH}_2^+$ (m/z 71, rearrangement in analogy to that observed for cycloalkanols). Loss of methanol to give hydrocarbon fragments, $\text{C}_n\text{H}_{2n-2}$ (m/z 54, 68, 82,...).

Fragmentation of ethyl and higher alkyl ethers of cycloalkanols with > 3 C atoms: Alkene elimination to yield the protonated cycloalkanol (m/z 72, 86, 100,...) and heterolytic cleavage of the C–O bond to give dominating cycloalkyl ions (m/z 69, 83,...).

Ion series: Besides the fragments already mentioned, mainly unsaturated hydrocarbon fragments ($\text{C}_n\text{H}_{2n-1}$, m/z 27, 41, 55, 69,...).

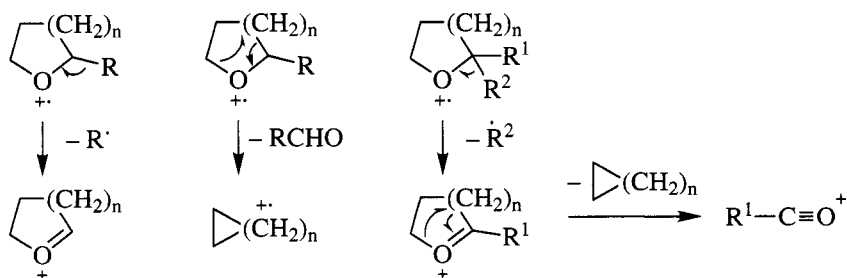
Intensities: The above mentioned fragments dominate the spectrum.

Molecular ion: Weak or intermediate.

7.8.11

Cyclic Ethers

Fragmentation: Primary ring cleavage at C–C bonds next to the O atom, followed by loss of CH_2O (Δm 30), H_2O (Δm 18), or alkyl (Δm 15, 29,...). Elimination of H^+ to give $[\text{M}-1]^+$, followed by CO elimination (Δm 28) to $[\text{M}-29]^+$. When α -substituted, dominant loss of substituents, followed by water elimination. Formation of acyl if two α -substituents are present.



Ion series: Mainly ions of the alkene type. Weak saturated, oxygen-containing fragments (m/z 31, 45,...).

Intensities: Intensive peaks evenly distributed over whole mass range.

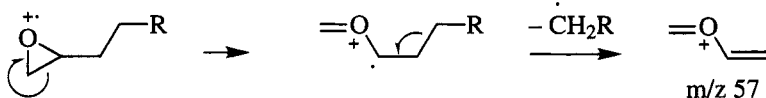
Molecular ion: Often significant but sometimes weak, especially when α -substituted. Intensity of $[\text{M}-1]^+$ usually comparable to that of $\text{M}^{+\cdot}$ if no α -substituent is present.

7.8.12

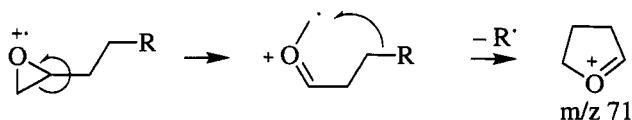
Aliphatic Epoxides [8]

Fragmentation: The most important primary fragmentation is the cleavage of C–C bonds next to the O atom (α -cleavage), resulting in complex degradation due to the related multiple choice and extensive secondary rearrangements. The products allow mass-spectrometric localization of double bonds after epoxidation.

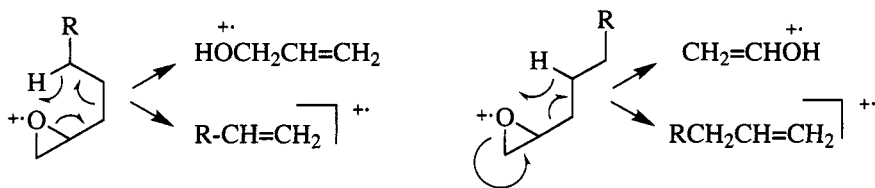
Due to ring opening prior to fragmentation, β -cleavage is as relevant as the α -cleavage.



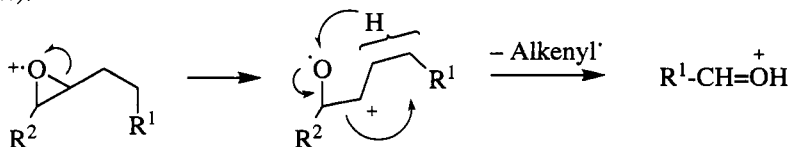
γ -Cleavage is the most important fragmentation mechanism, especially in terminal epoxides:



Mainly in terminal epoxides, rearrangement with alkene elimination, formally leading to alkene- $\text{OH}^{+\cdot}$ ($\text{C}_n\text{H}_{2n}\text{O}$, m/z 44, 58, 72,...) and alkene $^{+\cdot}$ (C_nH_{2n} , m/z 28, 42, 56,...):



Mainly in nonterminal epoxides, transannular cleavage with H transfer and elimination of an alkenyl radical, leading to $\text{C}_n\text{H}_{2n+1}\text{O}$ fragments (m/z 45, 59, 73,...):



Ion series: Mixed, not characteristic.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Usually weak.

7.8.13

Methoxybenzenes

Fragmentation: Loss of methyl radical, followed by decarbonylation to give $[M-43]^+$; elimination of formaldehyde (Δm 30) from M^{++} or from primary fragments.

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks in the M^{++} region.

Molecular ion: Strong.

7.8.14

Alkyl Aryl Ethers [9]

Fragmentation: Commonly dominating alkene elimination to give the corresponding phenol ion (non-specific hydrogen migration), followed by decarbonylation. In the case of aryl methyl ethers, loss of CH_2O from M^{++} or from primary fragments as well as $CH_3\cdot$ elimination followed by decarbonylation.

Ion series: Mostly aromatic hydrocarbon fragments, C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Usually maximum at the mass of the corresponding phenol. Otherwise, intensive peaks mainly concentrated in the high and medium mass range.

Molecular ion: Strong.

○

7.8.15

Aromatic Ethers

Fragmentation: Loss of $H\cdot$ (Δm 1), CO (Δm 28), and $CHO\cdot$ (Δm 29) from M^{++} . Cleavage at the C–O bond and decarbonylation of the resulting product, followed by dehydrogenation.

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

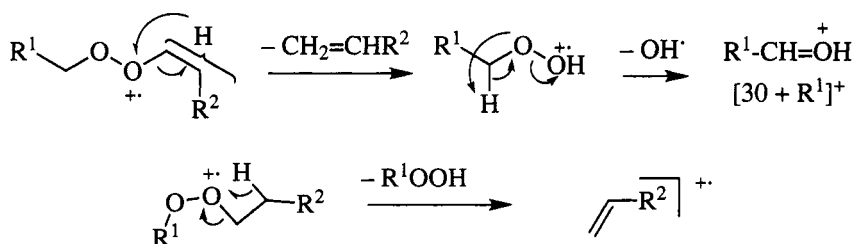
Intensities: Intensive peaks mainly in the M^{++} region.

Molecular ion: Strong.

7.8.16

Aliphatic Peroxides [4]

Fragmentation: Alkene elimination to give hydroperoxide radical cations and hydroperoxide elimination to yield alkene radical cations (dominating if larger alkyl groups are present). Alkene elimination can be followed by loss of $OH\cdot$, resulting in products that formally correspond to those obtained by O–O cleavage, which probably is not a one-step process (see scheme).



Elimination of O^\cdot or O_2 may occur in cyclic peroxides. *tert*-Butyl peroxides predominantly eliminate *tert*-butyl- OO^\cdot to give $[\text{M}-89]^+$.

Ion series: Saturated or unsaturated alkyl groups ($\text{C}_n\text{H}_{2n+1}$, m/z 29, 43, 57,...; $\text{C}_n\text{H}_{2n-1}$, m/z 27, 41, 55,...) and alkenyl ions (C_nH_{2n} , m/z 28, 42, 56,...) dominate. The fragment at m/z 31, and sometimes its homologues, indicate the presence of oxygen.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Weak to moderate.

7.8.17

References

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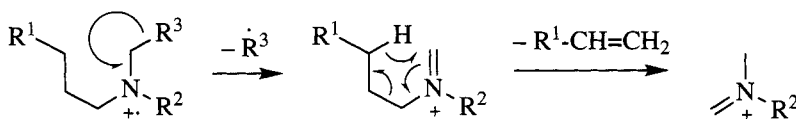
7.9

Nitrogen Compounds [1,2]

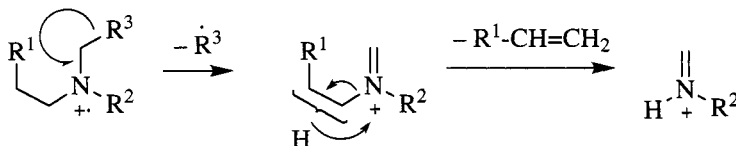
7.9.1

Saturated Aliphatic Amines [3]

Fragmentation: Dominating loss of alkyl residues by cleavage of the C–C bond next to the N atom (“N-cleavage”). Larger substituents are eliminated preferably. When a γ -H is available, subsequent elimination of alkenes by McLafferty-type reactions.



Otherwise, unspecific H transfer onto the N atom.



NH_3 , RNH_2 , and $\text{RR}'\text{NH}$ eliminations from primary, secondary, and tertiary amines, respectively, are negligible except from some multifunctional compounds (e.g., diamines and phenyl-phenoxy-substituted amines).

Ion series: Even-mass fragments of the type $\text{C}_n\text{H}_{2n+2}\text{N}$ (m/z 30, 44, 58, 72, 86, ...).

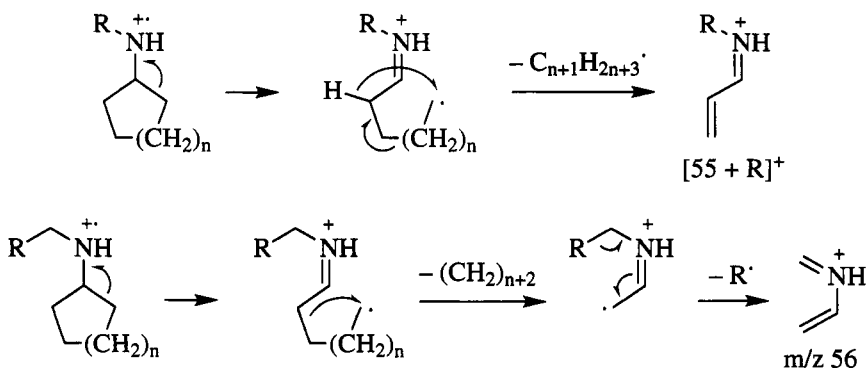
Intensities: Mainly peaks in the low mass range. Dominating base peak from “N-cleavage” at $[28 + m(\text{R}^1) + m(\text{R}^2) + m(\text{R}^4) + m(\text{R}^5)]^+$ for $\text{R}^1\text{R}^2\text{R}^3\text{CNR}^4\text{R}^5$ (e.g., m/z 30 for RCH_2NH_2 , m/z 44 for $\text{RCH}_2\text{NHCH}_3$, m/z 58 for $\text{RCH}_2\text{N}(\text{CH}_3)_2$, and m/z 86 for $\text{RCH}_2\text{N}(\text{CH}_2\text{CH}_3)_2$). Local maximum at m/z 86 ($\text{C}_5\text{H}_{12}\text{N}^+$) for n -alk- NH_2 (protonated piperidine, 6-membered ring).

Molecular ion: Usually weak or absent, especially if the α -C atom is substituted. Decreasing intensity with increasing molecular weight. Tendency to protonate to $[\text{M}+\text{H}]^+$.

7.9.2

Cycloalkylamines

Fragmentation: The most important primary reaction is the ring cleavage next to the N atom, followed by H rearrangement and loss of an alkyl residue. Some elimination of amine, $\text{R}_1\text{R}_2\text{NH}$.



Ion series: Even-mass fragments of the type $\text{C}_n\text{H}_{2n}\text{N}$ (m/z 42, 56, 70, 84,...).

Intensities: Intensive local maxima evenly distributed over whole mass range.

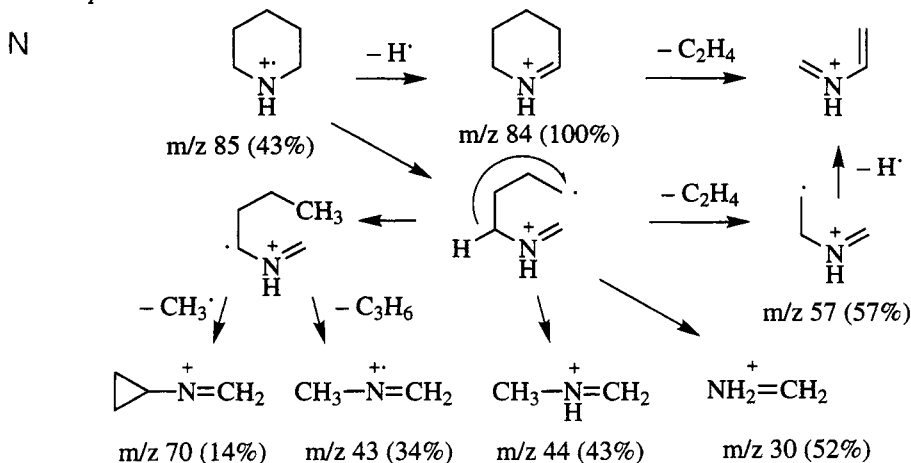
Molecular ion: Usually significant.

7.9.3

Cyclic Amines

Fragmentation: Dominating primary reaction is the cleavage of C–C bonds next to N, resulting in loss of substituents next to N or in primary ring cleavage. Primary ring cleavage is followed by H rearrangement and loss of alkenes or alkyl groups. The most important primary fragmentation for substituted cyclic amines is the loss of substituents at C atoms next to N.

Piperidine:



Ion series: Even-mass fragments of the type $\text{C}_n\text{H}_{2n}\text{N}$ (m/z 42, 56, 70, 84,...) and $\text{C}_n\text{H}_{2n+2}\text{N}$ (m/z 30, 44, 58,...) as well as odd-mass fragments of the type $\text{C}_n\text{H}_{2n+1}\text{N}$ (m/z 43, 57, 71, 85,...).

Intensities: Intensive local maxima evenly distributed over whole mass range if no substituent is bonded to the C atom next to N. Otherwise, dominating maxima by loss of such substituents.

Molecular ion: Significant or strong if no substituent is bonded to the C atom next to N; otherwise weak. Tendency to form $[M-H]^+$.

7.9.4

Piperazines

Fragmentation: As for cyclic amines, enhanced primary ring cleavage at C–C bonds next to the N atom.

Ion series: Even-mass fragments of the type $C_nH_{2n}N$ (m/z 42, 56, 70, 84,...) and $C_nH_{2n+2}N$ (m/z 30, 44, 58,...) as well as odd-mass series of the type $C_nH_{2n+1}N$ (m/z 43, 57, 71, 85,...).

Intensities: Intensive local maxima evenly distributed over whole mass range if no substituent is bonded to the C atom next to N. Otherwise, dominating maxima by loss of such substituents.

Molecular ion: Significant or strong if no substituent is bonded to the C atom next to N; otherwise weak. Tendency to form $[M-H]^+$.

7.9.5

Aromatic Amines

Fragmentation: Dominating cleavage of alkyl bond at N-bearing C atom (“N-cleavage”) followed by alkene elimination if aliphatic substituents with $\geq C_2$ are present. Otherwise, loss of H^\bullet from primary and secondary anilines and benzylic amines. Loss of HCN from M^+ or from fragments. A local maximum at m/z 42 is typical of an aromatically bonded dimethylamino group.

Ion series: Aromatic hydrocarbon fragments (C_nH_n and $C_nH_{n\pm 1}$; m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Dominating maxima by “N-cleavage” and following alkene loss if aliphatic substituents with $C_{n>1}$ are present.

Molecular ion: Abundant if no aliphatic substituents with more than one carbon atom are present, otherwise medium or weak. No tendency to protonate. In primary and secondary aromatic and benzylic amines, $[M-H]^+$ is important.

7.9.6

Aliphatic Nitro Compounds

Fragmentation: Loss of NO^\bullet (Δm 30), NO_2^\bullet (Δm 46), and HNO_2 (Δm 47) as well as the formation of some m/z 30 as \bar{N} indicator. Spectra with only few characteristic features.

Ion series: Mixed alkyl and alkenyl fragments, C_nH_{2n+1} (m/z 43, 57, 71,...) and C_nH_{2n-1} (m/z 41, 55, 69,...).

Intensities: Dominant peaks in the lower mass range.

Molecular ion: Weak or missing.

7.9.7

Aromatic Nitro Compounds

Fragmentation: Loss of O (Δm 16), NO \cdot (Δm 30, followed by elimination of CO, Δm 28), and NO $_2\cdot$ (Δm 46) from M $^{+\cdot}$ or from a major primary cleavage product. Extensive rearrangement of the functional group to a nitroso ester.

Ion series: Aromatic hydrocarbon fragments corresponding to C $_n$ H $_n$ and C $_n$ H $_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks mainly in the upper mass range.

Molecular ion: Strong.

7.9.8

Diazo Compounds [4,5]

Diazonium: Because of the low volatility of diazo compounds, their electron impact mass spectra show thermal decomposition products. These are formed by loss of N $_2$ (e.g., an aromatic chloro compound is formed from the corresponding diazonium chloride). From a phenyl diazonium *ortho*-carboxylate zwitterion, biphenylene is formed as dimerization product.

Diazomethane and derivatives: M $^{+\cdot}$ is strong except when catalytic decomposition occurs on metal surfaces of the inlet system. Loss of N $_2$ is a dominant reaction of diazomethane and diazoketones.

N

7.9.9

Azobenzenes

Fragmentation: Cleavage at the azo group followed by loss of N $_2$, giving rise to the dominant base peak.

Ion series: Aromatic hydrocarbon fragments corresponding to C $_n$ H $_n$ and C $_n$ H $_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Dominant M $^{+\cdot}$ and azo cleavage products.

Molecular ion: Strong.

7.9.10

Aliphatic Azides [6]

Fragmentation: [M-42] $^{+}$ (N $_3\cdot$ elimination) or [M-28] $^{+\cdot}$ (N $_2$ elimination) is dominant in most cases. The spectra have the character of the corresponding aliphatic compounds.

Ion series: Aliphatic hydrocarbon series.

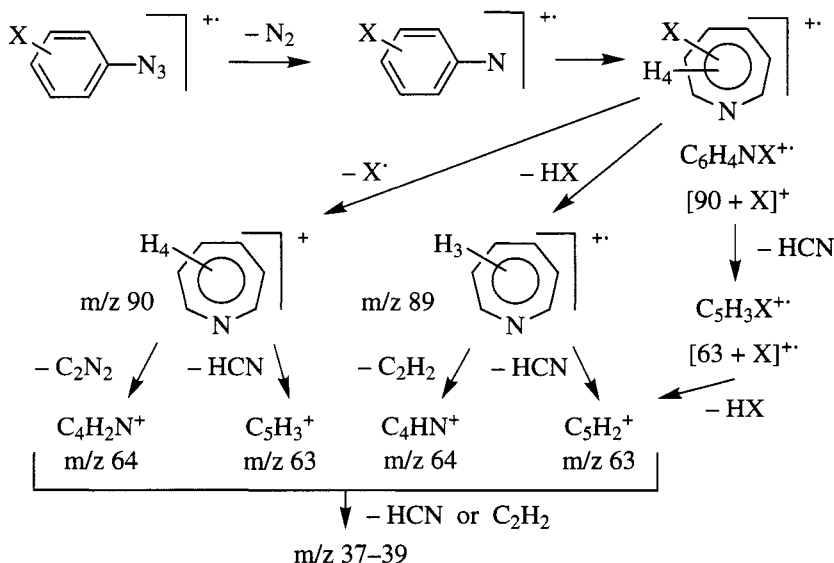
Intensities: Dominant peaks in the lower mass range, as in aliphatic compounds.

Molecular ion: Absent or weak. Odd mass for odd number of N atoms in the molecule.

7.9.11

Aromatic Azides [7]

Fragmentation: In most cases, $[M-28]^+$ (N_2 elimination) is the base peak. The next step is the elimination of HCN (Δm 27) or acetylene (Δm 26), or, if there is a substituent X on the ring, of X^\cdot or HX.



N

Ion series: Aromatic hydrocarbon fragments (C_nH_n and $C_nH_{n\pm 1}$; m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Dominant peaks in the higher mass range: $[M-28]^+$ (N_2 elimination) and $[M-55]^+$ (N_2 and HCN elimination) are the most intense peaks.

Molecular ion: Weak. Odd mass for odd number of N atoms in the molecule.

7.9.12

Aliphatic Nitriles [4]

Fragmentation: Elimination of alkyl radicals to give $(CH_2)_nCN^+$ ions (m/z 40, 54, 68,...). McLafferty rearrangement yielding $CR_2=C=NH^+$ (m/z 41 for R: H). In most cases, C–CN cleavage and HCN elimination are not significant reactions. Complex rearrangements in unsaturated cyanides if other functional groups are present.

Ion series: Saturated and unsaturated alkyl ions mainly in the lower mass range (C_nH_{2n+1} and C_nH_{2n-1} ; m/z 29, 43, 57,... and 27, 41, 55,...). Rearrangement products corresponding to $C_nH_{2n-1}N$ contribute, to a significant extent, to the ion series m/z 41, 55, 69,... For alkyl chains with $C_{n>5}$, dominating $(CH_2)_nCN^+$ (i.e., $C_nH_{2n-2}N$, m/z 82, 96, 110,..., probably with a cyclic structure).

Intensities: Intensive peaks due to the above mentioned ions.

Molecular ion: Weak or missing. Both $[M+H]^+$ and $[M-H]^+$ are usually more intense than $M^{+\bullet}$. In some aliphatic nitriles, $[M+2H]^{++}$ is as intensive as $M^{+\bullet}$. Odd mass for odd number of N atoms in the molecule.

7.9.13

Aromatic Nitriles

Fragmentation: Consecutive elimination of HCN and acetylene.

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks in the M^+ region.

Molecular ion: Dominant intensity, often base peak. In contrast to aliphatic and benzylic nitriles, $[M-1]^+$ is usually not important. Odd mass for odd number of N atoms in the molecule.

7.9.14

Aliphatic Isonitriles (R–NC)

Fragmentation: In general, the spectra are similar to those of the corresponding nitriles. The most important difference lies in the loss of CN^{\bullet} (Δm 26) and the higher probability of losing HCN (Δm 27). Further important fragmentations are the elimination of alkyl radicals to give $(CH_2)_nCN^+$ ions and the McLafferty rearrangement to yield $CR_2=N=CH^{+\bullet}$ (m/z 41 if R: H).

Ion series: Saturated and unsaturated alkyl ions mainly in the lower mass range (C_nH_{2n+1} , m/z 29, 43, 57,... and C_nH_{2n-1} , m/z 27, 41, 55,...). Rearrangement products corresponding to $C_nH_{2n-1}N$ contribute, to a significant extent, to the ion series of m/z 41, 55, 69,...

Intensities: Intensive peaks in the lower mass range.

Molecular ion: Weak, decreasing with increasing chain length and degree of branching. Both $[M+H]^+$ and $[M-H]^+$ can be stronger than $M^{+\bullet}$. Odd mass for odd number of N atoms in the molecule.

7.9.15

Aromatic Isonitriles (R–NC) [4]

Fragmentation: Dominant loss of HCN ($[M-27]^{+\bullet}$). In methylphenyl and benzyl isocyanides also formation of isocyanotropylium ion, $[M-1]^+$, followed by loss of HCN to $[M-28]^+$.

Ion series: Aromatic hydrocarbon fragments (C_nH_n and $C_nH_{n\pm 1}$; m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks in the higher mass range.

Molecular ion: Dominant; base peak for phenyl isocyanide. Odd mass for odd number of N atoms in the molecule.

7.9.16

Aliphatic Cyanates (R-OCN) [8]

Fragmentation: Spectra often very similar to those of the corresponding isocyanates. Cleavage of the C–C bond next to O, with the charge remaining on $\cdot CH_2OCN$ (m/z 56) for short-chain cyanates and preferably on the alkyl substituent if it has a $C_{n>2}$ chain (m/z 29, 43, 57,...). Cleavage of the C–O bond with H rearrangement to give $HCNO^{+\cdot}$ (m/z 43) or $alkene^{+\cdot}$ (m/z 42, 56, 70,...). For cyanates with $C_{n>5}$ substituents, alkene elimination to yield m/z 99.

Ion series: Saturated and unsaturated alkyl cations (C_nH_{2n+1} , m/z 29, 43, 57,... and C_nH_{2n-1} , m/z 27, 41, 55,...). Alkene radical cations (C_nH_{2n} , m/z 42, 56, 70,...) together with isobaric ions of the composition $C_nH_{2n}NCO$.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Usually weak or absent. $[M-H]^+$ is often more intense. Odd mass for odd number of N atoms in the molecule.

7.9.17

Aromatic Cyanates (R-OCN) [8]

Fragmentation: Loss of $OCN\cdot$ (Δm 42) or, to a lesser extent, of CO, with subsequent HCN elimination (Δm 28 and 27).

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks in the higher mass range.

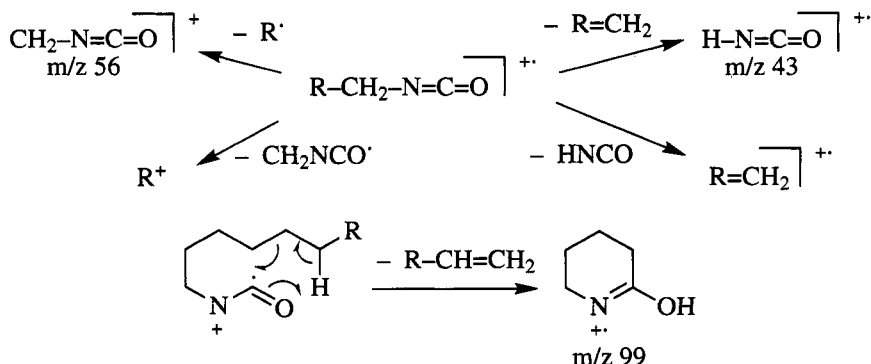
Molecular ion: Strong. Odd mass for odd number of N atoms in the molecule.

7.9.18

Aliphatic Isocyanates (R-NCO) [8]

Fragmentation: Spectra often very similar to those of the corresponding cyanates. Cleavage of the C–C bond next to N, the charge remaining on the $\cdot CH_2NCO$ (m/z 56) for short-chain isocyanates and preferably on the alkyl substituent for compounds with a $C_{n>2}$ chain (m/z 29, 43, 57,...). Cleavage of the C–N bond with H rearrangement to give $HCNO^{+\cdot}$ (m/z 43) or $alkene^{+\cdot}$ (m/z 42, 56, 70,...) ions. For isocyanates with $C_{n>5}$ alkyl chains, alkene elimination, yielding m/z 99.

N



Ion series: Saturated and unsaturated alkyl cations ($\text{C}_n\text{H}_{2n+1}$, m/z 29, 43, 57,... and $\text{C}_n\text{H}_{2n-1}$, m/z 27, 41, 55,...). Alkene radical cations (C_nH_{2n} , m/z 42, 56, 70,...) together with isobaric ions of the composition of $\text{C}_n\text{H}_{2n}\text{OCN}$.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Usually weak or absent. $[\text{M-H}]^+$ is often more intense. Odd mass for odd number of N atoms in the molecule.

7.9.19

Aromatic Isocyanates (R-NCO) [8]

Fragmentation: Consecutive elimination of CO (Δm 28) and HCN (Δm 27). In contrast to aromatic cyanates, practically no elimination of $\text{NCO}\cdot$ (Δm 42).

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks in the higher mass range.

Molecular ion: Dominating; base peak for phenyl isocyanate. Odd mass for odd number of N atoms in the molecule.

7.9.20

Aliphatic Thiocyanates (R-SCN) [8]

Fragmentation: Elimination of HCN (Δm 27) followed by loss of an alkyl group. The cleavage of the C–C bond next to SCN is unimportant except in short-chain thiocyanates.

Ion series: Saturated and unsaturated alkyl cations ($\text{C}_n\text{H}_{2n+1}$, m/z 29, 43, 57,... and $\text{C}_n\text{H}_{2n-1}$, m/z 27, 41, 55,...).

Intensities: Intensive peaks in the lower mass range.

Molecular ion: Weak. Decreasing with increasing chain length and degree of branching; absent from the spectrum of hexyl thiocyanate. Odd mass for odd number of N atoms in the molecule. Both $[\text{M+H}]^+$ and $[\text{M-H}]^+$ are detectable.

Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\cdot}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\cdot}$).

7.9.21

Aromatic Thiocyanates ($\text{R}-\text{SCN}$) [8]

Fragmentation: The most important fragmentation is the elimination of SCN^{\cdot} (Δm 58). Further elimination reactions are loss of CN^{\cdot} (Δm 26), HCN (Δm 27), and CS (Δm 44).

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...). Weak signal at m/z 45 (CHS^+) indicates sulfur.

Intensities: Intensive peaks in the higher mass range.

Molecular ion: Dominant; base peak in phenyl thiocyanate. Odd mass for odd number of N atoms in the molecule. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\cdot}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\cdot}$).

7.9.22

Aliphatic Isothiocyanates ($\text{R}-\text{NCS}$) [8]

Fragmentation: Cleavage of the C–C bond next to NCS, leading to m/z 72 (CH_2NCS) or to its homologues if the α -C atom is substituted. Loss of the alkyl residue with concomitant double hydrogen rearrangement to yield the protonated functional group (m/z 60). With a $\text{C}_{n>4}$ alkyl chain, loss of SH^{\cdot} (Δm 33). With $\text{C}_{n>5}$ alkyl chain, loss of alkene leading to m/z 115, probably according to the mechanism shown for isocyanates.

Ion series: Mainly saturated and unsaturated alkyl cations ($\text{C}_n\text{H}_{2n+1}$, m/z 29, 43, 57,... and $\text{C}_n\text{H}_{2n-1}$, m/z 27, 41, 55,...). Signal for CH_2NCS^+ (m/z 72) or its homologues (m/z 86, 100, 114,...) if the α -C atom is substituted.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Medium to weak, decreasing with increasing chain length and degree of branching. More intense than in the corresponding thiocyanates; 1% for hexadecyl isothiocyanate. Both $[\text{M}+\text{H}]^+$ and $[\text{M}-\text{H}]^+$ are relevant. Odd mass for odd number of N atoms in the molecule. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\cdot}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\cdot}$).

7.9.23

Aromatic Isothiocyanates ($\text{R}-\text{NCS}$) [8]

Fragmentation: Dominant loss of NCS^{\cdot} (Δm 58). In contrast to aromatic thiocyanates, the loss of HCN (Δm 27) or CS (Δm 44) leads to very weak fragments only.

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...). Weak signal at m/z 45 (CHS^+) indicates sulfur.

N

Intensities: Intensive peaks in the higher mass range.

Molecular ion: Dominant; base peak in phenyl isothiocyanate. Odd mass for odd number of N atoms in the molecule. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{++}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to M^{++}).

7.9.24

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7.10

Sulfur-Containing Functional Groups [1]

7.10.1

Aliphatic Thiols [2]

Fragmentation: Elimination of H_2S (Δm 34; or SH , Δm 33, from secondary thiols) followed by loss of alkenes; consecutive losses of ethylene from unbranched thiols. Cleavage of the $\alpha, \beta\text{-C-C}$ bond (next to the SH group) leads to CH_2SH^+ (m/z 47). Note that this fragment also occurs in secondary and tertiary thiols. The S atom is poorer than N, but better than O, at stabilizing such a fragment. Cleavage at the next C-C bonds leads to signals at m/z 61, 75, and 89. In secondary and tertiary thiols, prominent fragments are formed by loss of the largest α -alkyl group.

Ion series: Dominant consecutive alkenyl fragments ($\text{C}_n\text{H}_{2n-1}$, m/z 41, 55, 69,...) and smaller aliphatic fragments ($\text{C}_n\text{H}_{2n+1}$, m/z 43, 57, 71,...). Sulfur-containing aliphatic fragments: $\text{C}_n\text{H}_{2n+1}\text{S}$ (m/z 47, 61, 75, 89,...). Often significant sulfur-indicating fragments: HS^+ , H_2S^+ , H_3S^+ , and CHS^+ (m/z 33, 34, 35, and 45).

Intensities: More intensive peaks in the lower mass range; mostly of the alkene type. Characteristic local maxima from S-containing fragments, $\text{C}_n\text{H}_{2n+1}\text{S}$ (m/z 47, 61, 75, 89,...). In n -alkyl thiols, the intensity of m/z 61 is roughly half that of m/z 47; the signal at m/z 89 is more intense than that at m/z 75, presumably because it is stabilized by cyclization.

Molecular ion: Relatively strong except for higher tertiary thiols. Characteristic ^{34}S isotope peak at $[\text{M}+2]^+$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to M^+).

7.10.2

Aromatic Thiols [2]

S

Fragmentation: CS elimination from M^+ and $[\text{M}-1]^+$, yielding $[\text{M}-44]^+$ and $[\text{M}-45]^+$. SH elimination from M^+ to give $[\text{M}-33]^+$.

Ion series: HCS^+ (m/z 45) is characteristic besides the aromatic fragments, C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

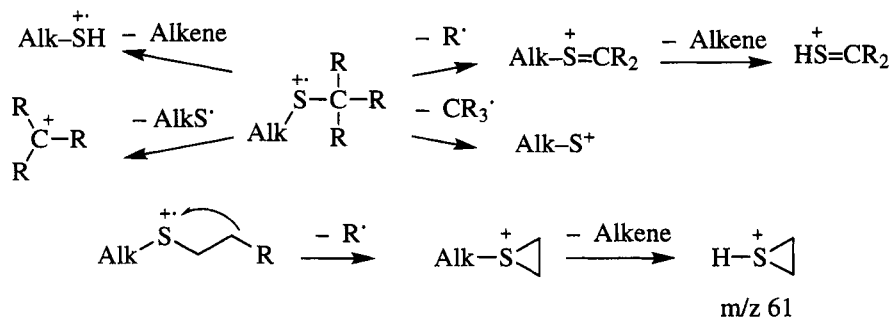
Intensities: Intensive peaks in the higher mass range.

Molecular ion: Usually dominating; base peak in thiophenol. $[\text{M}-1]^+$ is usually strong. Characteristic ^{34}S isotope peak at $[\text{M}+2]^+$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to M^+).

7.10.3

Aliphatic Sulfides [1]

Fragmentation: Loss of alkyl radicals by cleavage of the C–C bond next to S (the largest group being lost preferably) and of the C–S bond, followed by alkene and H₂S elimination. Alkene elimination from M⁺⁺ to form the corresponding thiol ions. In contrast to thiols and cyclic sulfides, no H₂S or HS[•] elimination from M⁺⁺.



In general, the H rearrangements are non-specific. Secondary H transfer predominates over primary H transfer.

Ion series: Sulfur-containing aliphatic fragments, C_nH_{2n+1}S (m/z 47, 61, 75, 89,...). The hydrocarbon fragments may dominate in long-chain sulfides.

Intensities: Intensive peaks in the lower mass range. Characteristic local maxima from S-containing fragments, C_nH_{2n+1}S (m/z 47, 61, 75, 89,...).

Molecular ion: Usually strong. Characteristic ³⁴S isotope peak at [M+2]⁺⁺ and [Frag+2]⁺ for S-containing fragments (per S atom 4.4% relative to M⁺⁺).

7.10.4

S Alkyl Vinyl Sulfides

Fragmentation: Loss of alkyl radicals (Δm 15, 29, 43,...). Elimination of thioethanol (Δm 62) after triple H rearrangement. Dominant m/z 60 (CH₃CH=S⁺) accompanied by m/z 61 (CH₃CH₂S⁺).

Ion series: Sulfur-containing unsaturated aliphatic fragments, C_nH_{2n-1}S (m/z 45, 59, 73,...). Unsaturated hydrocarbon ions, C_nH_{2n} (m/z 42, 56, 70,...) and C_nH_{2n-2} (m/z 40, 54, 68,...)

Intensities: Intensive peaks evenly distributed over the whole mass range.

Molecular ion: Of medium intensity. Characteristic ³⁴S isotope peak at [M+2]⁺⁺ and [Frag+2]⁺ for S-containing fragments (per S atom 4.4% relative to M⁺⁺).

7.10.5

Cyclic Sulfides [3]

Fragmentation: Primary cleavage of the C–C bond next to S, followed by rearrangements and elimination of CH_3^\cdot (base peak for tetrahydrothiapyrane) and $\text{C}_2\text{H}_5^\cdot$. In tetrahydrothiophene, $[\text{M}-1]^+$ is also significant. HS^\cdot , H_2S , and C_2H_4 elimination from $\text{M}^{+\cdot}$.

Ion series: Sulfur-containing aliphatic fragments with one degree of unsaturation, $\text{C}_n\text{H}_{2n-1}\text{S}$ (m/z 45, 59, 73, 87, 101,...), m/z 87 being of special dominance.

Intensities: Overall distribution of peaks maximizing in the low mass range due to S-containing fragments, $\text{C}_n\text{H}_{2n-1}\text{S}$ (m/z 45, 59, 73, 87,...).

Molecular ion: Very strong. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\cdot}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\cdot}$).

7.10.6

Aromatic Sulfides [2]

Fragmentation: Loss of CS (Δm 44) and of HS (Δm 33) from $\text{M}^{+\cdot}$.

Ion series: HCS^+ (m/z 45) is characteristic besides the aromatic fragments, C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks mainly in the higher mass range.

Molecular ion: Strong. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\cdot}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\cdot}$).

7.10.7

Disulfides

Fragmentation: Loss of RSS^\cdot leading to alkyl cations and alkene elimination to give $\text{RSSH}^{+\cdot}$. Cleavage of the S–S bond with or without H rearrangements, leading to RS^+ , $[\text{RS}-\text{H}]^{+\cdot}$, and $[\text{RS}-2\text{H}]^+$. Loss of one or two S with or without H atoms is a common process in cyclic, unsaturated, and aromatic disulfides.

Ion series: In saturated aliphatic disulfides, H_2S_2 and its alkyl homologues are characteristic (m/z 66, 80, 94,...).

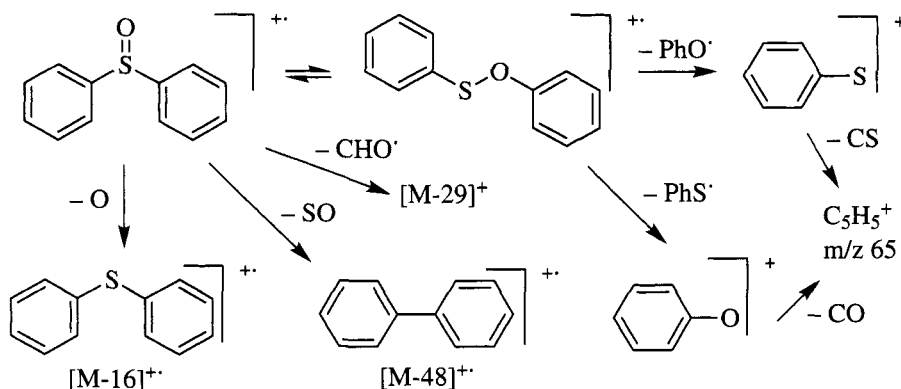
Intensities: Variable.

Molecular ion: Usually strong. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\cdot}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\cdot}$).

S

The skeletal rearrangement is not relevant for the fragmentation of higher alkyl aryl sulfoxides. Here, direct cleavage of the C–S bonds and McLafferty rearrangements dominate.

For diaryl sulfoxides, elimination of SO (to give $[M-48]^{+}$) as well as of O, OH \cdot , and COH \cdot (yielding $[M-16]^{+}$, $[M-17]^{+}$, and $[M-29]^{+}$). After rearrangement to sulfenates, fragmentation of the S–O bond to produce ar–S $^{+}$ and ar–O $^{+}$ ions, which further lose CS and CO, respectively, to give C₅H₅ $^{+}$ (m/z 65).



Ion series: Besides the ions described under *Fragmentation*, mainly fragments of the aromatic type, i.e., C_nH_n and C_nH_{n±1} (m/z 39, 51–53, 63–65, 75–77,...), as well as O- and S-containing ions.

Intensities: Intensive peaks mainly in the high mass range.

Molecular ion: Very strong. Characteristic ³⁴S isotope peak at $[M+2]^{+}$ and $[Frag+2]^{+}$ for S-containing fragments (per S atom 4.4% relative to M $^{+}$).

7.10.10

Aliphatic Sulfones [4,5]

S

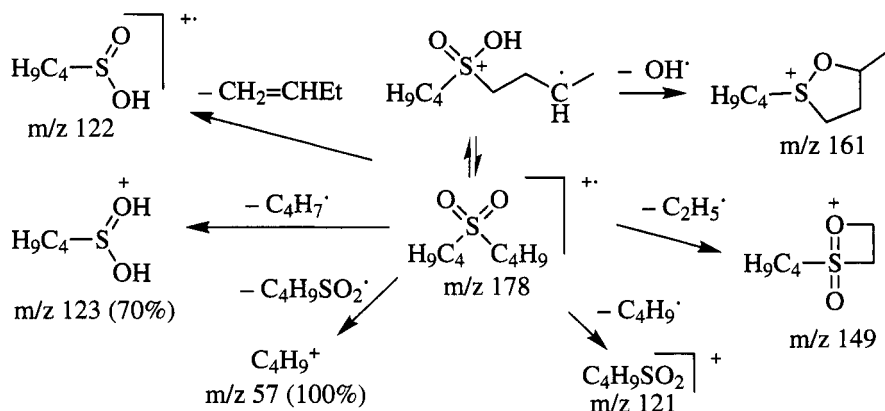
Fragmentation: Fragmentation of the S–C bond with the charge remaining on either side. Single and double H rearrangements to give RS(O)OH $^{+}$ and RS(OH) $_2^{+}$.

The probability of the double H rearrangement increases with increasing chain length. If one of the substituents is unsaturated, rearrangement to RS(O)O-alkene and fragmentation of the S–O bond yields the ion RSO $^{+}$.

Ion series: Dominating aliphatic fragments, C_nH_{2n+1} (m/z 29, 43, 57,...) and C_nH_{2n-1} (m/z 27, 41, 55,...). Usually one significant fragment corresponding to alk–S(O)OH $^{+}$ (from the series of m/z 80, 94, 108,...) or alk–S(OH) $_2^{+}$ (from the series of m/z 81, 95, 109,...) can be observed.

Intensities: Intensive peaks mainly aliphatic fragments in the lower mass range.

Molecular ion: Weak. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\bullet}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\bullet}$).



7.10.11

Cyclic Sulfones [4]

Fragmentation: Dominant eliminations of SO_2 (Δm 64, followed by loss of CH_3^\bullet), HSO_2^\bullet (Δm 65, followed by loss of C_2H_4), or CH_2SO_2 (Δm 78). Weak fragment at $[\text{M}-17]^+$ due to OH^\bullet elimination.

Ion series: Mainly unsaturated hydrocarbon fragments, $\text{C}_n\text{H}_{2n-1}$ (m/z 27, 41, 55,...).

Intensities: Intensive peaks in the lower mass range.

Molecular ion: Moderate. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{+\bullet}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to $\text{M}^{+\bullet}$).

S

7.10.12

Alkyl Aryl Sulfones [4]

Fragmentation: Isomerization of $\text{M}^{+\bullet}$ to $\text{ar}-\text{OS}(=\text{O})\text{alk}$ and formation of the phenoxy ion or the phenol radical cation with H rearrangement. The migration of the aryl group depends on the type of substituents. It is facilitated by electron donors and hindered by acceptors. Mainly in substituted or unsaturated alkyl derivatives also isomerization to $\text{ar}-\text{S}(=\text{O})\text{O}-\text{alk}(\text{ene})$ and formation of $\text{ar}-\text{S}=\text{O}^+$ (m/z 125 if ar is phenyl). Single and double H rearrangements to give $\text{ar}-\text{S}(\text{O})\text{OH}^{+\bullet}$ and $\text{ar}-\text{S}(\text{OH})_2^+$. The probability of the double H rearrangement increases with increasing chain length. In some derivatives, SO_2 elimination from $\text{M}^{+\bullet}$ dominates. Substituents X of the alkyl group may migrate to the aryl group to yield $\text{X}-\text{ar}-\text{S}=\text{O}^+$ ions.

Ion series: Aromatic fragments, C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...), as well as S- and O-containing aromatic fragments at higher masses.

Intensities: Intensive peaks mainly in the higher mass range.

Molecular ion: Strong. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{++}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to M^{++}).

7.10.13

Diaryl Sulfones [4,5]

Fragmentation: Predominant aromatic fragments of the type ar-O^+ and ar-SO^+ (m/z 125 if ar is phenyl), formed after migration of one of the aryl groups. The ar-SO_2^+ ion is unimportant; ar^+ is intense. Small fragments due to SO_2 , SO_2H^+ , and SO_2H_2 eliminations (Δm 64, 65, and 66, respectively). With alkyl substituents in *ortho* position, $[\text{M-OH}]^+$ and $[\text{M-H}_2\text{O}]^{++}$ are formed, upon which SO elimination follows.

Ion series: Aromatic fragments, C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...) and the S- and O-containing aromatic fragments at higher masses. Usually, ar-SO^+ (m/z 125 if ar is phenyl) is very strong.

Intensities: Intensive peaks mainly in the higher mass range.

Molecular ion: Strong. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{++}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to M^{++}).

7.10.14

Aromatic Sulfonic Acids [6]

Fragmentation: The most prominent fragment, $[\text{M-HSO}_3]^+$ (Δm 81), is formed in a two-step process. In the first step, OH $^\cdot$ elimination leads to a weak fragment ion $[\text{M-OH}]^+$ (Δm 17). If an alkyl group is present in *ortho* position, $[\text{M-H}_2\text{SO}_3]^{++}$ (Δm 82) is formed instead of $[\text{M-81}]^+$. Other important fragments are $[\text{M-SO}_2]^+$ (Δm 64), $[\text{M-HSO}_2]^+$ (Δm 65), and $[\text{M-SO}_3]^+$ (Δm 80).

Ion series: Aromatic fragments, C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...), and O-containing aromatic fragments at higher masses.

Intensities: Intensive peaks mainly in the higher mass range.

Molecular ion: Very strong. Characteristic ^{34}S isotope peak at $[\text{M}+2]^{++}$ and $[\text{Frag}+2]^+$ for S-containing fragments (per S atom 4.4% relative to M^{++}).

7.10.15

Alkylsulfonic Acid Esters [6]

Fragmentation: Loss of alkyl by fragmentation of the C–O bond with concomitant double H rearrangement to form the protonated sulfonic acid ion (m/z 97 for methanesulfonates), which then loses water. Loss of the alkoxyl residue (fragmentation of the S–O bond). Formation of an alkene ion from the sulfonate alkyl by a McLafferty-type rearrangement. In aryl esters, the phenoxy ion and the phenol radical cations dominate the spectrum.

Ion series: Besides RSO_3H_2^+ and RSO_2^+ (m/z 97 and 79 for methanesulfonates), for aliphatic esters mainly alkene fragments. In aryl esters, aromatic fragments,

S

C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...), as well as O-containing aromatic fragments at higher masses.

Intensities: Intensive peaks in the lower mass range.

Molecular ion: Small or negligible in alkyl esters; strong in aryl esters. Characteristic ^{34}S isotope peak at $[M+2]^{+}$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to M^{+}).

7.10.16

Arylsulfonic Acid Esters [6]

Fragmentation: Dominating fragments resulting from cleavage of the S–O bond (leading to the $ar-SO_2^+$ ion), which loses SO_2 (m/z 155 and 91 for *p*-toluenesulfonates). In alkylsulfonates with longer chains, double H rearrangement to give the protonated acid (m/z 173 for *p*-toluenesulfonates).

Ion series: Aromatic fragments, C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...).

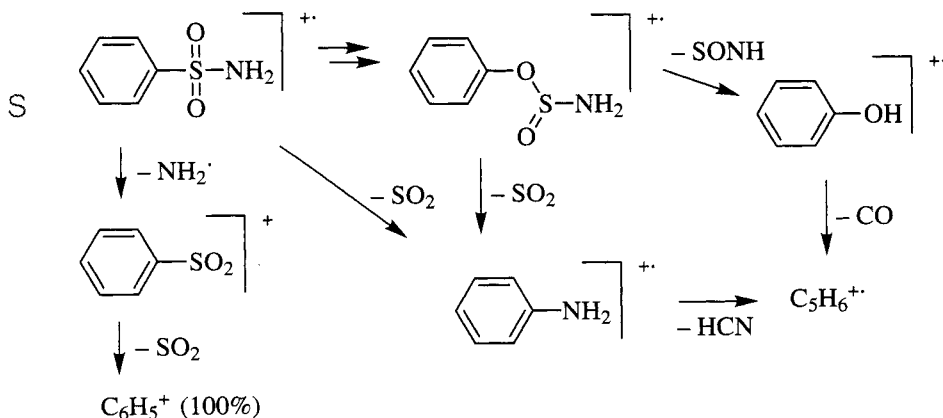
Intensities: Intensive peaks mainly in higher mass range.

Molecular ion: Medium or weak. Characteristic ^{34}S isotope peak at $[M+2]^+$ and $[Frag+2]^+$ for S-containing fragments (per S atom 4.4% relative to M^{+}).

7.10.17

Aromatic Sulfonamides [6]

Fragmentation: In *N*-alkylamides, the C–C bond next to N is split preferably. In *N*-arylamides, besides $[M-SO_2]^{+}$ and $[M-HSO_2]^+$, the ions $ar-SO_2^+$ and $ar'-NH^+$ are formed.



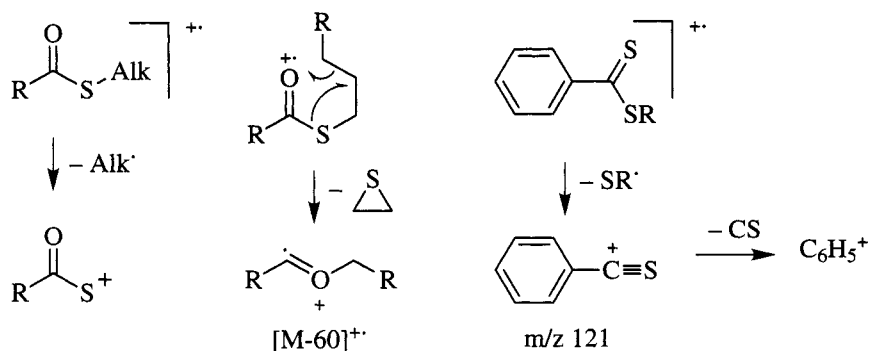
Ion series: Ions typical of the tosyl group: m/z 155, 91, and 65.

Molecular ion: In arylamides, M^{+} is dominant.

7.10.18

Thiocarboxylic Acid S-Esters [7]

In contrast to esters, elimination of the alkyl radical from the thiol site is the major fragmentation process. Ethylene sulfide is eliminated from thioesters with longer alkyl chains. Aromatic dithiocarboxylic acid esters usually fragment in two steps to the aryl cation.



7.10.19

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7.11

Carbonyl Compounds [1-4]

7.11.1

Aliphatic Aldehydes [5]

Fragmentation: Cleavage of the bond next to CO. The fragmentation of the hydrocarbon chain is similar to that in corresponding alkanes. McLafferty rearrangement with localization of the charge on either side, giving rise to $C_nH_{2n}^{+}$ (m/z 28, 42, 56,...) and, often less important, to $C_nH_{2n}O^{+}$ ions (m/z 44, 58, 72,...). At least one product (often both) is significant. Elimination of water from the molecular ion to give $[M-18]^{+}$, occasionally very pronounced.

Ion series: Dominating consecutive fragments of the series of C_nH_{2n+1} and $C_nH_{2n-1}O$ (in both cases: m/z 29, 43, 57,...). Weaker fragments of the series C_nH_{2n-1} (m/z 41, 55, 69,...) and rearrangement products, C_nH_{2n} (m/z 28, 42, 56,...).

Intensities: Intensive peaks concentrated in the lower mass range. Local even-mass maxima from McLafferty-type reactions ($[M-44]^{+}$ when aldehyde not substituted in α -position).

Molecular ion: Only strong for molecules of low molecular weight; very weak for $C_{n>9}$. $[M-1]^{+}$ may be more relevant than M^{+} .

7.11.2

Unsaturated Aliphatic Aldehydes

Fragmentation: Cleavage of the bond next to CO, leading to $[M-1]^{+}$ (more significant than in saturated aldehydes), $[M-29]^{+}$, and m/z 29. No McLafferty rearrangement occurs if the γ -hydrogen atom is attached to a double bond or if there is a double bond in α,β -position.

Ion series: Fragments of the series of C_nH_{2n-1} and $C_nH_{2n-3}O$ (in both cases m/z 41, 55, 69,...).

Molecular ion: Stronger than in saturated aldehydes. Usually, $[M-1]^{+}$ is relevant.

C = X

7.11.3

Aromatic Aldehydes

Fragmentation: Characteristic H^{\cdot} loss to yield the corresponding benzoyl ion, $[M-1]^{+}$, followed by decarbonylation to a phenyl ion, $[M-1-28]^{+}$, of lower intensity. To a small extent also decarbonylation of the molecular ion, leading to $[M-28]^{+}$. Weak signal at m/z 29 (CHO^{+}).

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks predominantly in the molecular ion region.

Molecular ion: Usually prominent. $[M-1]^{+}$ is strong.

7.11.4

Aliphatic Ketones

Fragmentation: Cleavage of the bond next to CO is the most important primary fragmentation. The charge can remain on either side. The acyl ions then lose CO. McLafferty rearrangement giving rise to $C_nH_{2n}O^{+}$ ions (m/z 58, 72, 86,...). Consecutive rearrangements occur if both alkyl chains contain a γ -H atom. Keto-enol tautomerism of the first rearrangement product is not a prerequisite for the second rearrangement to occur. Oxygen is sometimes indicated by weak signals at $[M-18]^+$ and m/z 31, 45, 59. Fragmentation of the hydrocarbon chain similar to that in the corresponding alkanes.

Ion series: Dominating consecutive fragments of the series C_nH_{2n+1} and $C_nH_{2n-1}O$ (in both cases: m/z 29, 43, 57,...), with maxima due to cleavage at the CO group to give acyl ions and their decarbonylation products. Weaker fragments in the series C_nH_{2n-1} (m/z 41, 55, 69,...). Even-mass maxima, $C_nH_{2n}O$ (m/z 58, 72, 86,...), due to alkene elimination (McLafferty rearrangement). Usually, m/z 43 (CH_3CO^+) is strong if an unsubstituted α - CH_2 group is present.

Intensities: Intensive peaks mainly in the lower mass range.

Molecular ion: Relatively abundant, weak in long-chain and branched aliphatic ketones.

7.11.5

Unsaturated Ketones

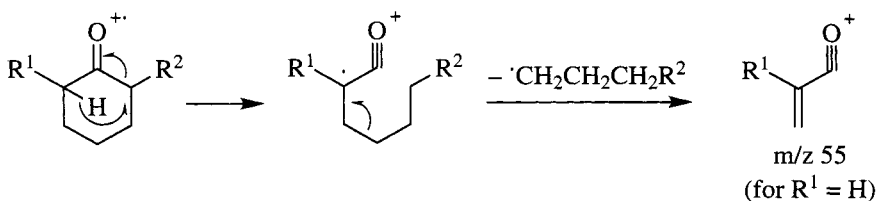
Fragmentation: Cleavage of the bond next to CO, more favorably on the saturated side, is the most important primary fragmentation. The acyl ion then loses CO. The McLafferty rearrangement occurs neither when the unsaturated substituents are in α,β position nor when the only available γ -hydrogen atom is attached to a double-bonded carbon.

Molecular ion: Relatively abundant.

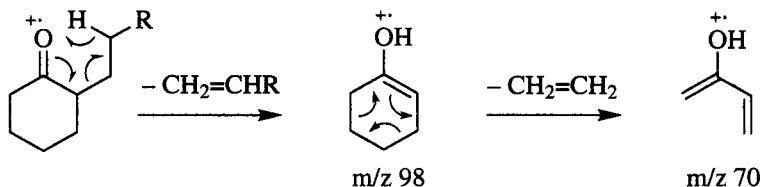
7.11.6

Alicyclic Ketones

Fragmentation: Major primary fragmentation by bond cleavage next to carbonyl, followed by loss of alkyl residue. $C=X$



Prominent McLafferty-type elimination of larger alkyl groups in position 2 or 6 as alkenes. This rearrangement is very favorable; even aromatically bonded H atoms can rearrange. For cyclohexanones, a consecutive retro-Diels–Alder reaction can occur:



Oxygen is sometimes indicated by a weak signal at $[\text{M}-18]^+$.

Ion series: Consecutive alkene fragments of the type of $\text{C}_n\text{H}_{2n-1}$ or $\text{C}_n\text{H}_{2n-3}\text{O}$ (for both: m/z 41, 55, 69,...) with maxima due to alkyl loss after ring opening next to the carbonyl group and H transfer. Prominent even-mass maxima by elimination of substituents at position 2 or 6 as alkenes via sterically favored McLafferty rearrangements.

Intensities: Overall more intensive peaks in the lower mass range or even distribution of major peaks over the whole mass range. Local maxima from major fragmentation pathway.

Molecular ion: Abundant.

7.11.7

Aromatic Ketones

Fragmentation: Dominant α -cleavage to give the benzoyl ion, followed by decarbonylation to a phenyl ion of lower intensity. α -Cleavage in acetophenone also produces the acetyl cation (m/z 43). Even-mass maxima due to alkene elimination via McLafferty rearrangement. CO elimination from diaryl ketones through skeletal rearrangements.

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and C_nH_{n+1} (m/z 39, 51–53, 63–65, 75–77,...).

$\text{C}=\text{X}$ **Intensities:** Intensive peaks predominantly in the molecular ion region.

Molecular ion: Strong.

7.11.8

Aliphatic Carboxylic Acids

Fragmentation: Fragmentation of the C–CO bond leading to m/z 45 and to $[\text{M}-45]^+$. Loss of OH^\cdot leading to $[\text{M}-17]^+$; may be followed by decarbonylation. Cleavage of the γ bond (relative to CO) leading to $^+\text{CH}_2\text{CH}_2\text{COOH}$ (m/z 73) if there is no branching on the α - and β -C atoms. Loss of H^\cdot (not the carboxylic one) leading to $[\text{M}-1]^+$. Water elimination to give $[\text{M}-18]^+$ if the alkyl group

consists of at least 4 C atoms; may be followed by decarbonylation. McLafferty rearrangement to m/z 60 (acetic acid) if there is no α -substituent.

Ion series: Saturated and unsaturated alkyl ions mainly in the lower mass range (C_nH_{2n+1} and C_nH_{2n-1} , m/z 29, 43, 57,... and 27, 41, 55,...). With long-chain aliphatic acids, $C_nH_{2n-1}O_2$ series (m/z 59, 73, 87,...), exhibiting maxima for $n = 3, 7, 11, 15, \dots$ (m/z 73, 129, 185, 241,...). Even-mass maxima, $C_nH_{2n}O_2$ (m/z 60, 74, 88,...), due to McLafferty rearrangements.

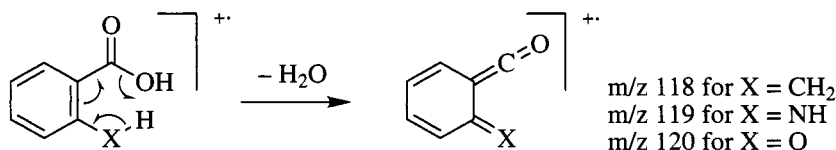
Intensities: Intensive peaks due to the above mentioned ions.

Molecular ion: Generally detectable. Easily protonated to $[M+H]^+$.

7.11.9

Aromatic Carboxylic Acids

Fragmentation: Pronounced loss of OH^\cdot , leading to $[M-17]^+$ and followed by decarbonylation (Δm 28) to a phenyl ion of lower intensity. Water elimination to $[M-18]^+$ if a H-bearing *ortho*-substituent is present. Some acids decarboxylate (Δm 44). Loss of CO (Δm 28) from $M^{+\cdot}$.



Ion series: Aromatic hydrocarbon fragments, C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks predominantly in the molecular ion region.

Molecular ion: Strong.

7.11.10

Carboxylic Acid Anhydrides

Fragmentation: In the case of linear anhydrides abundant acyl ions due to cleavage next to carbonyl group. For cyclic anhydrides maxima due to decarboxylation (Δm 44), followed by decarbonylation.

$C = X$

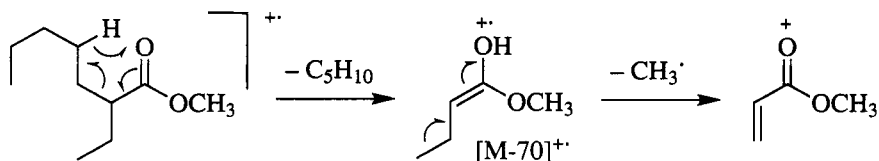
Molecular ion: Weak or absent (especially in linear aliphatic anhydrides), easily protonated to $[M+H]^+$. Relatively strong for phthalic anhydrides.

7.11.11

Saturated Aliphatic Esters

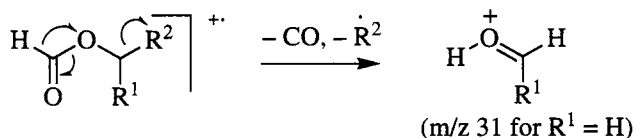
Fragmentation: Dominant fragmentation of the bonds next to the carbonyl C, leading to $alk-CO^+$ (m/z 43, 57, 71,...; decreasing intensity with increasing length of the alkyl chain) and followed by decarbonylation, as well as fragmentation to $COOR^+$ (m/z 59, 73, 87,...) and to alk^+ (m/z 15, 29, 43,...).

Alcohol elimination to $C_nH_{2n-2}O$ (m/z 42, 56, 70,...), followed by decarbonylation (Δm 28) or ketene elimination (Δm 42). Alkene elimination from the acid side via McLafferty rearrangements, leading to $C_nH_{2n}O_2$ (m/z 60, 74, 88,...). The larger alkyl group participates in the rearrangement if several γ -H atoms are available. In the following example, the alternative process leading to $[M-C_2H_4]^+$ is negligible.



Non-specific H rearrangements at the alcohol side (from M^{++} or the McLafferty product) lead to $C_nH_{2n}O_2$ and to the corresponding alkene, C_nH_{2n} (m/z 28, 42, 56,...). In methyl esters of long chain acids, the ions $[(CH_2)_{2+4n}COOCH_3]^+$ (m/z 87, 143, 199,...) correspond to maxima. For esters of higher alcohols (at least C_3), double H rearrangement to the protonated acid, $C_nH_{2n+1}O_2$ (m/z 61, 75, 89,...). α -Substituted esters may lose the substituent and then CO (Δm 28) via alkoxyl rearrangement. In an analogous reaction, β -substituted esters may eliminate ketene (Δm 42).

Besides usual ester reactions, specific rearrangements can be observed in formates.



Ion series: C_nH_{2n+1} (m/z 29, 43, 57,...) for the alkyl groups at the ester oxygen (except for methyl esters). C_nH_{2n-1} (m/z 27, 41, 55,...). $C_nH_{2n-1}O_2$ (m/z 59, 73, 87,...), exhibiting maxima for $n = 4, 8, 12, \dots$ (m/z 87, 143, 199,...) in case of the methyl esters of long-chain acids. Even-mass maxima for $C_nH_{2n}O_2$ (m/z 60, 74, 88,...) due to alkene elimination via McLafferty rearrangements on both sides of the carboxyl group. C_nH_{2n} (m/z 28, 42, 56,...) as H rearrangement product from the alcohol side.

C = X

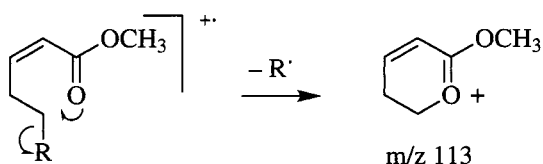
Intensities: Intensive peaks due to above mentioned ions from the lower mass range.

Molecular ion: Often of low abundance. Easily protonated to $[M+H]^+$.

7.11.12

Unsaturated Esters

α,β -Unsaturated esters: Loss of $alk-O\cdot$ followed by $C=O$ elimination is the dominant fragmentation path. Also, loss of the δ -substituent yields a 6-membered oxonium ring:

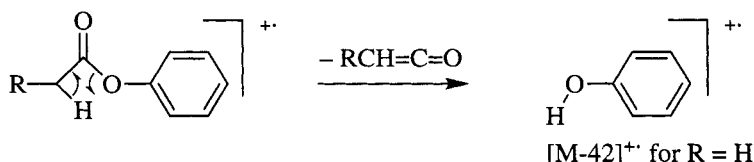


Significant difference between Z and E isomers of long-chain α,β -unsaturated esters: Single H rearrangement occurs with Z esters and double H rearrangements (leading to protonated acids) have been found for E esters.

β,γ -Unsaturated esters: Only slight qualitative, but significant quantitative differences have been observed as compared to α,β -unsaturated esters.

γ,δ -Unsaturated esters: Loss of the alcohol chain as a radical, R' , followed by ketene elimination.

Aliphatic enol esters and aryl esters: Formation of alk-CO^+ ($m/z\ 43, 57, 71, \dots$). Elimination of a ketene to give the enol/phenol radical cation. The rearrangement occurs predominantly, but not exclusively, through a 4-membered transition state.



7.11.13

Esters of Aromatic Acids

Fragmentation: Dominant loss of RO^\cdot to form the benzoyl ion, followed by decarbonylation ($\Delta m\ 28$) and further loss of acetylene ($\Delta m\ 26$). Ethyl esters also eliminate C_2H_4 ($\Delta m\ 28$) to give the acid radical cation, which then loses OH^\cdot to yield the benzoyl ion. In higher alkyl esters, besides the acid, the protonated acid is formed (double H rearrangement). In *ortho*-substituted aryl esters with an α -hydrogen atom on the substituent, an alcohol is eliminated from $\text{M}^{+\cdot}$. In the case of alkyl phthalates (other than dimethyl phthalate), alkenyl elimination to give the protonated ester acid, followed by alkene elimination from the other ester group, and subsequently water elimination to the protonated anhydride ion, which forms the base peak at $m/z\ 149$.

$\text{C}=\text{X}$

Ion series: Aromatic hydrocarbon fragments, C_nH_n and $\text{C}_n\text{H}_{n\pm 1}$ ($m/z\ 39, 51-53, 63-65, 75-77, \dots$).

Intensities: Prominent maximum at the mass of the related benzoyl ion and its decarbonylation product.

Molecular ion: Usually strong.

7.11.14 Lactones

Fragmentation: The most prominent reaction is the loss of substituents (or H \cdot) at the O-bearing C atom, followed by decarbonylation (Δm 28), decarboxylation (Δm 44, mainly in smaller molecules), and ketene elimination (Δm 42). Decarboxylation of M^{++} is rarely significant. Competing reactions are several kinds of primary ring cleavages. Aromatic lactones show maxima due to two consecutive decarbonylations.

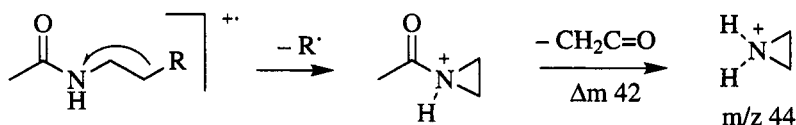
Ion series: No specific ion series. The acetyl ion (m/z 43) is often an important fragment.

Intensities: Maxima at the mass resulting from loss of substituents at the C atom next to oxygen. Otherwise, intensive peaks evenly distributed over whole mass range.

Molecular ion: Usually of low intensity and easily protonated to $[M+H]^+$ in aliphatic lactones; abundant in the case of aromatic lactones.

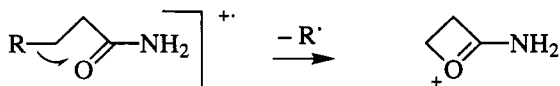
7.11.15 Aliphatic Amides

Fragmentation: Alkene elimination on the acid side via McLafferty reaction to yield the corresponding acetamide radical cation. Loss of alkenes on the amine side to give the ion of the desalkyl amide, often via double H rearrangement to the protonated desalkyl amide ion. Cleavage on both sides of the carbonyl group. Cleavage of the C–C bond attached to N, and the β,γ -C–C bond (relative to N; see scheme).



Cleavage of the bonds to the β -C (see scheme) and γ -C on the amine side.

C = X



Ion series: Even-mass fragments corresponding to $C_nH_{2n}NO$ (m/z 44, 58, 72,...) produced by cleavage of the bond next to CO on the acidic side. Odd-mass fragments (in secondary and tertiary amides), $C_nH_{2n-1}O$ (m/z 43, 57, 71,...), produced by cleavage of the bond next to CO on the amine side.

Intensities: Overall peak distribution maximizing in the low mass range. Local maxima from McLafferty and from γ -cleavage products.

Molecular ion: Significant. Strong tendency to protonate to $[M+H]^+$.

7.11.16**Amides of Aromatic Carboxylic Acids**

Fragmentation: Amides of aromatic acids exhibit maxima due to amide bond cleavage yielding the benzoyl ion, followed by decarbonylation (Δm 28).

Ion series: Aromatic hydrocarbon fragments corresponding to C_nH_n and $C_nH_{n\pm 1}$ (m/z 39, 51–53, 63–65, 75–77,...).

Intensities: Intensive peaks predominantly in the molecular ion region.

Molecular ion: Abundant. $[M-H]^+$ is significant in N,N-disubstituted anilides, weaker in monosubstituted derivatives, and absent from the spectrum of benzamide. It is formed exclusively by loss of *ortho*-hydrogens of the aromatic ring.

7.11.17**Anilides**

Formanilides: Loss of CO (Δm 28) to give the aniline radical cation and consecutive HCN elimination (Δm 27).

Acetanilides: Ketene elimination to yield the aniline radical cation (often base peak), which consecutively eliminates HCN (Δm 27), and formation of the acetyl cation (m/z 43).

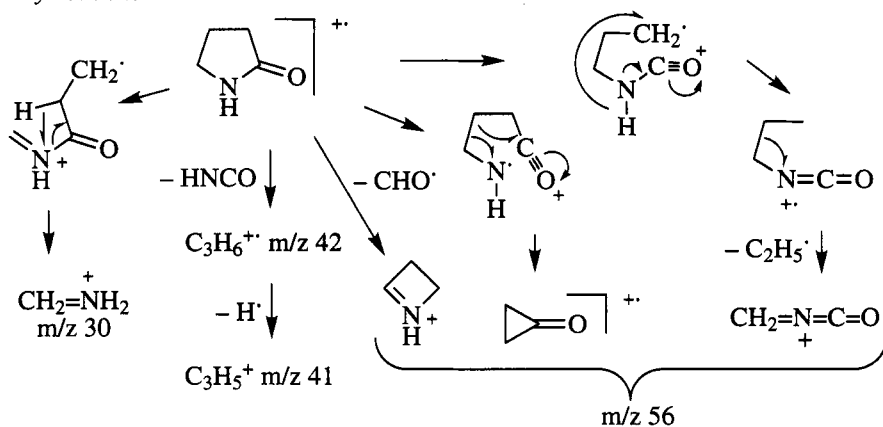
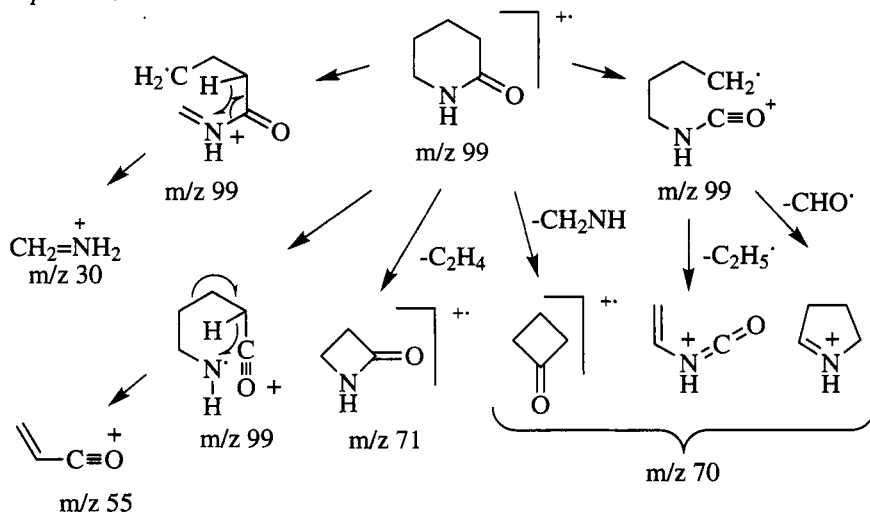
Trichloroacetanilides: Dominant loss of CCl_3^{\cdot} (Δm 117).

Pivalanilides: Besides reactions analogous to those of acetanilides (formation of the aniline radical cation, Δm 84), also formation of the *tert*-butylbenzene radical cation through elimination of HNCO (Δm 43).

7.11.18**Lactams**

Fragmentation: Cleavage of the C–C bond at the N-bearing C atom. Cleavage of the CO–N bond, followed by loss of CO (Δm 28) or by further cleavage of the C–C bond next to N, giving an iminium ion. In 2-pyrrolidone and 2-piperidone, the signal at m/z 30 ($[CH_2=NH_2]^+$) is strong. The base peak of 2-pyridone is formed by CO elimination (Δm 28).

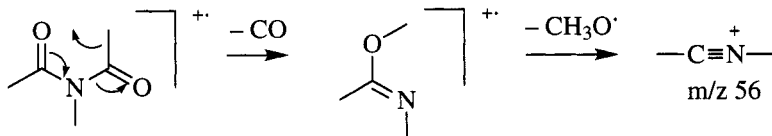
C = X

2-Pyrrolidone:*2-Piperidone:*

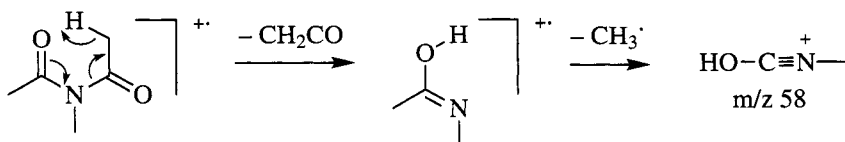
$\text{C}=\text{X}$ Molecular ion: Often observable; more abundant than for the corresponding lactones.

7.11.19 Imides

Saturated acyclic imides: Consecutive CO (Δm 28) and alkoxy elimination:

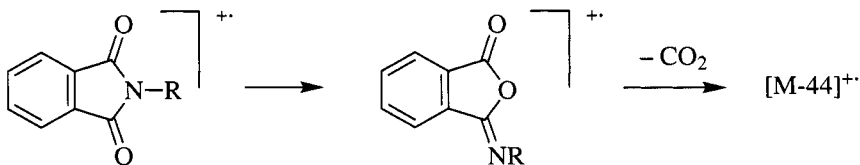


Ketene elimination:

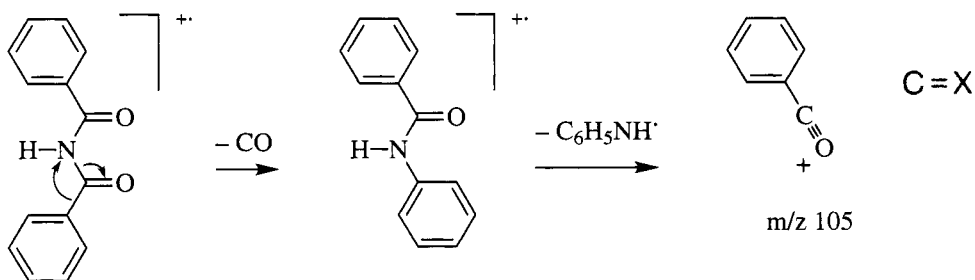


If the N-substituent chain is sufficiently long, cleavages of the C–C bond next to N with or without H rearrangement.

Cyclic imides: The spectra of saturated cyclic imides are almost identical to those of the corresponding diketones. Loss of HNCO (Δm 43) from succinimide, followed by CO elimination (Δm 28). Aroyl migration and loss of CO_2 from aromatic cyclic imides.



Dibenzoylamine: Loss of CO to *N*-phenylbenzamide:



7.11.20**References**

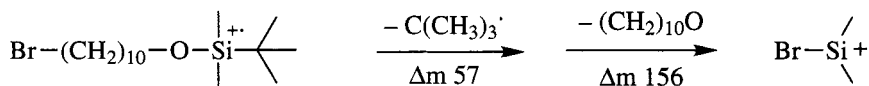
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- [4] D.G.I. Kingston, B.W. Hobrock, M.M. Bursey, J.T. Bursey, Intramolecular hydrogen transfer in mass spectra. III. Rearrangements involving the loss of small neutral molecules, *Chem. Rev.* **1975**, 75, 693.
- [5] A.G. Harrison, High-resolution mass spectra of aliphatic aldehydes, *Org. Mass. Spectrom.* **1970**, 3, 549.

C=X

7.12 Miscellaneous Compounds

7.12.1 Trialkylsilyl Ethers [1,2]

Fragmentation: Loss of alkyl attached to Si (preferential loss of larger groups). Cleavage of the C–C bond adjacent to O, followed by alkene elimination. Loss of alkoxy, followed by alkene eliminations. Elimination of trialkylsilanol. The R_2Si-OR' cation has the tendency to attack, in an electrophilic manner and even over long distances, free electron pairs and π -electron centers, causing the expulsion of neutral fragments from the interior of the molecule via a rearrangement:



Ion series: $[C_nH_{2n+3}OSi]^+$ (m/z 75, 89, 103, 117,...). $[C_nH_{2n+3}Si]^+$ (m/z 45, 59, 73, 87,...). Occasionally, maxima at even mass due to elimination of trialkylsilanol.

Molecular ion: $M^{+\cdot}$ often of low abundance or absent, easily protonated to $[M+H]^+$. Typical isotope patterns owing to ^{28}Si , ^{29}Si , and ^{30}Si (see Chapter 2.5.5).

7.12.2 Alkyl Phosphates [3]

Fragmentation: Maxima due to alkenyl loss from $M^{+\cdot}$ via double H rearrangement, followed by successive alkene eliminations down to protonated phosphoric acid (m/z 99).

Ion series: PO^+ (m/z 47), $H_2PO_2^+$ (m/z 65), $H_2PO_3^+$ (m/z 81), often as non-specific P indicators.

Molecular ion: $M^{+\cdot}$ observable.

7.12.3 Aliphatic Phosphines and Phosphine Oxides

Misc.

Ion series: Maxima of the ion series of $[C_nH_{2n+3}P]^+$ (m/z 48, 62, 76, 90,...) due to alkene eliminations.

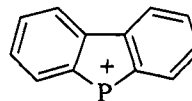
Molecular ion: $M^{+\cdot}$ observable.

7.12.4

Aromatic Phosphines and Phosphine Oxides

Fragmentation: Maxima due to loss of an aryl group, followed by H_2 elimination to yield the 9-phosphafluorenyl ion (m/z 183).

Molecular ion: $M^{+\cdot}$ abundant, easily losing H^\cdot to give $[M-1]^+$.



m/z 183

7.12.5

References

- [1] D.G.I. Kingston, B.W. Hobrock, M.M. Bursey, J.T. Bursey, Intramolecular hydrogen transfer in mass spectra. III. Rearrangements involving the loss of small neutral molecules, *Chem. Rev.* **1975**, 75, 693.
- [2] H. Schwarz, Positive and negative ion chemistry of silicon-containing molecules in the gas phase. In: *The Chemistry of Organic Silicon Compounds*; S. Patai, Z. Rappoport, Eds.; Wiley: Chichester, 1989; p 445.
- [3] D.G.I. Kingston, J.T. Bursey, M.M. Bursey, Intramolecular hydrogen transfer in mass spectra. II. The McLafferty rearrangement and related reactions, *Chem. Rev.* **1974**, 74, 215.

7.13

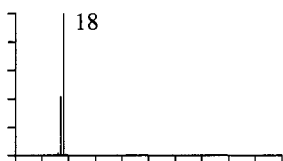
Mass Spectra of Common Solvents and Matrix Compounds

7.13.1

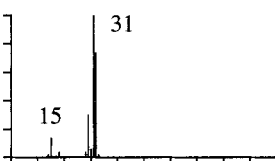
Electron Impact Ionization Mass Spectra of Common Solvents

The label {50} indicates that the intensity scale ends at 50% relative intensity and is subdivided in 10% steps. In these cases, the height of the base peak has to be doubled to bring it to 100%. All spectra represent positive ions only.

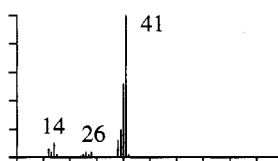
Water {50}



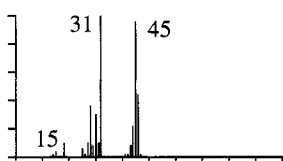
Methanol



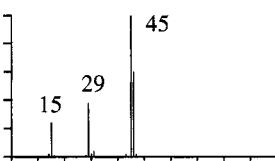
Acetonitrile



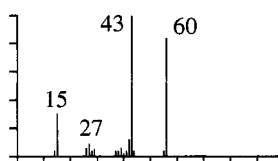
Ethanol {50}



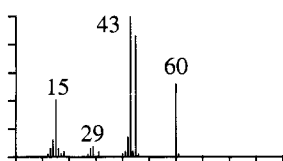
Dimethyl ether



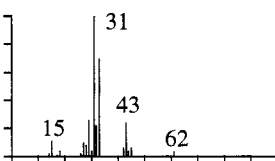
Acetone {50}



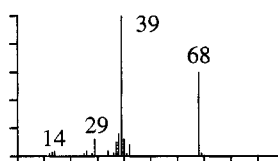
Acetic acid



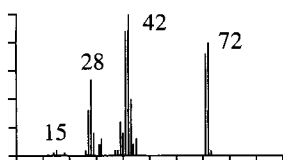
Ethylene glycol {50}



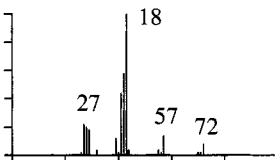
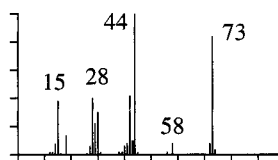
Furan



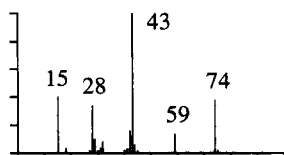
Tetrahydrofuran {50}



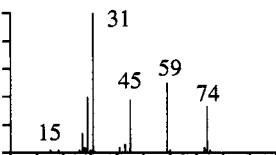
Pentane

*N,N*-Dimethylformamide

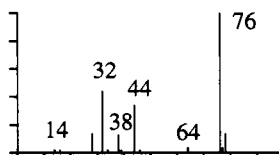
Methyl acetate {50}



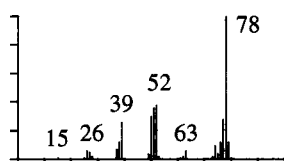
Diethyl ether



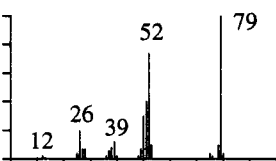
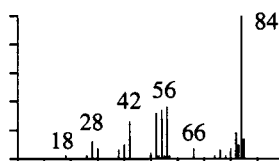
Carbon disulfide {50}



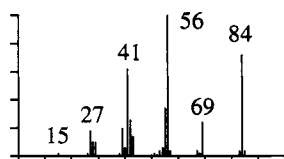
Benzene {50}



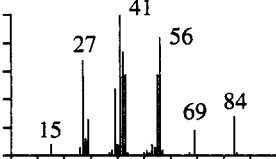
Pyridine

Benzene-*d*₆ {50}

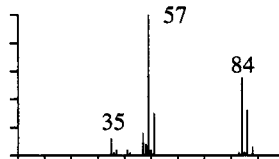
Cyclohexane



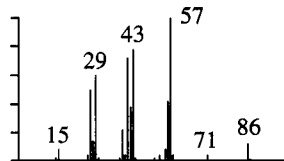
1-Hexene



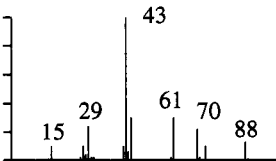
Methylene chloride



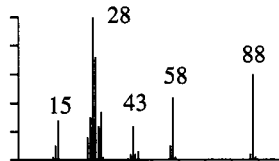
Hexane



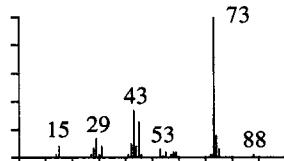
Ethyl acetate {50}



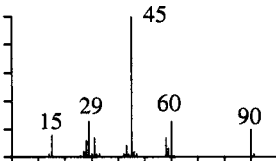
1,4-Dioxane {50}



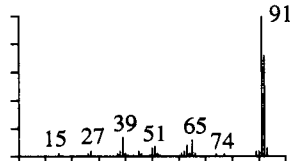
Tetramethylsilane {50}



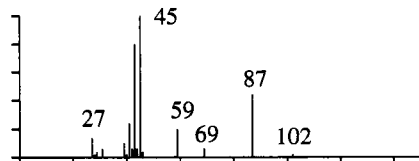
Dimethyl glycol {50}



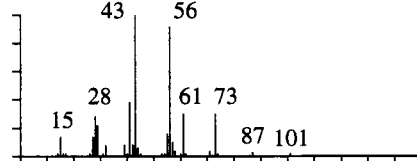
Toluene



Diisopropyl ether {50}

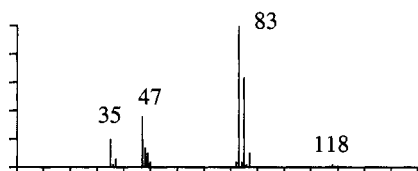
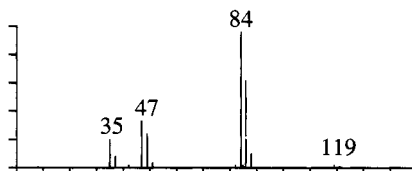


Butyl acetate {50}

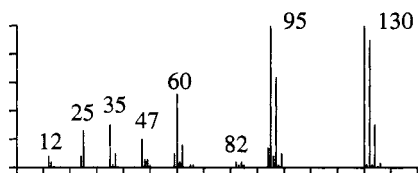


Solvents

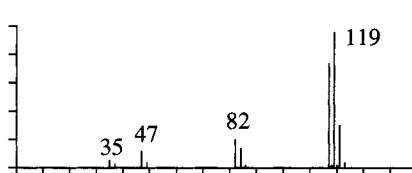
Chloroform

Chloroform-*d*

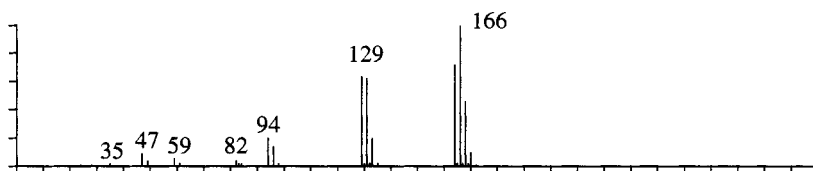
Trichloroethylene



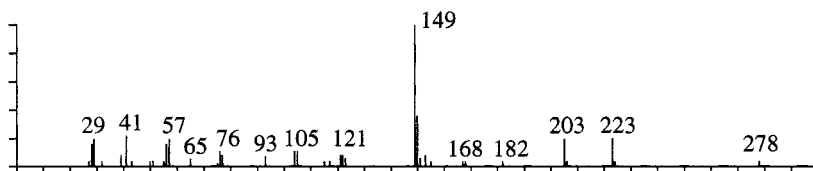
Carbon tetrachloride



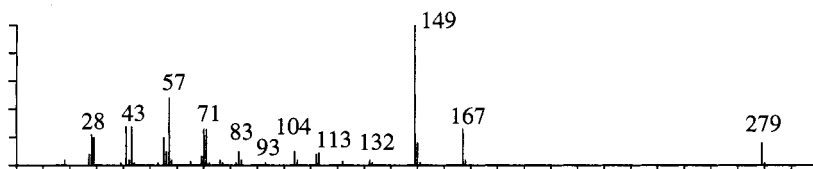
Tetrachloroethylene



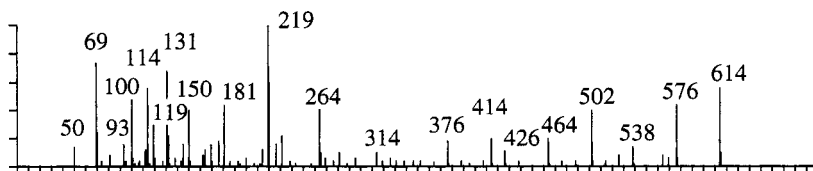
Dibutyl phthalate [25] (frequent impurity due to its use as polymer plasticizer)



Diethyl phthalate (frequent impurity due to its use as polymer plasticizer)



Heptacosfluorotributylamine (calibration reagent)



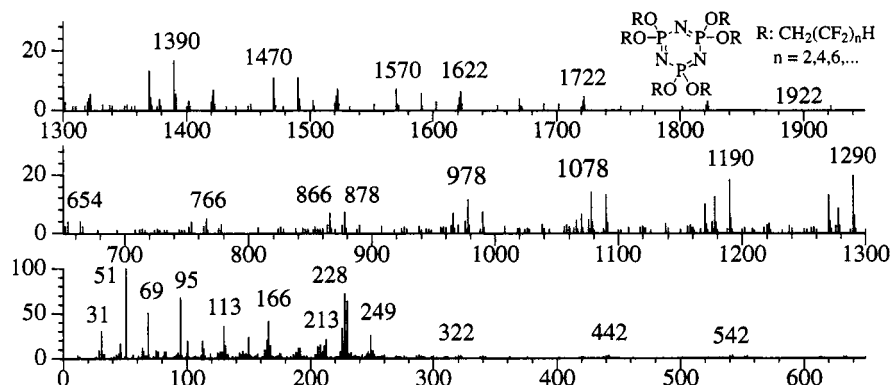
7.13.2

Spectra of Common FAB MS Matrix and Calibration Compounds

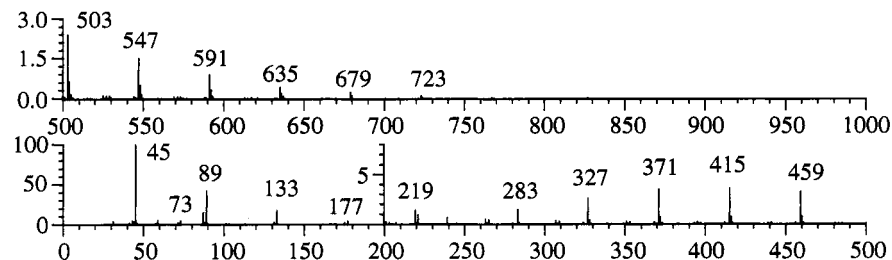
Fast atom bombardment (FAB) mass spectra (MS) usually exhibit protonated or deprotonated molecular ions, $[M \pm H]^\pm$, and protonated clusters, $[M_n + X_m \pm H]^\pm$ ($n, m = 0, 1, 2, \dots$), of the sample and matrix molecules, X. If there are even traces of metal salts in the sample, clusters of the type $[M_n + X_m + \text{metal cation}]^+$ occur in positive ionization mass spectra. Sodium (23 u) and potassium (39 u) ion adducts are most commonly encountered. The nature of the clusters is often revealed by the regular intervals at which they occur in the spectra.

Calibration Compounds in Positive Ionization FAB Mass Spectra

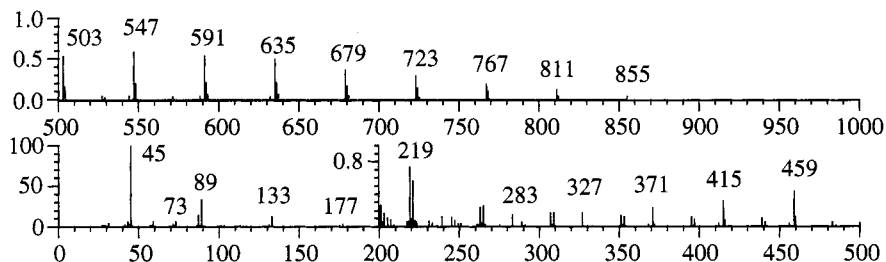
Ultramark 1621 (erroneously also referred to as "perfluoroalkyl phosphazine")



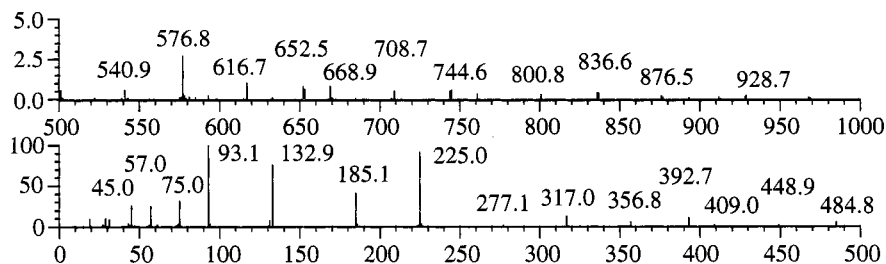
Polyethylene glycol 400 (often used as an internal reference for high resolution m/z determinations)



Polyethylene glycol 600 (often used as an internal reference for high resolution m/z determinations)

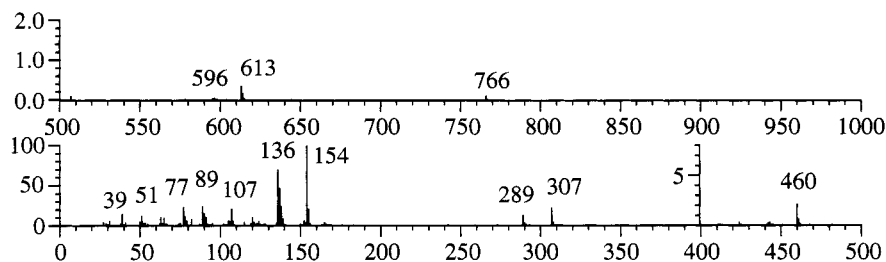


CsI (Cs^+ , 132.9; I^- , 126.9) in glycerol (formation of $[\text{glycerol}_m\text{-H}_n + \text{Cs}_p + \text{I}_q]^+$)

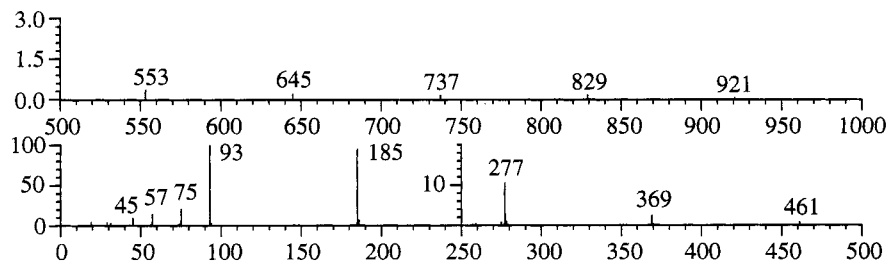


Matrix Compounds in Positive Ionization FAB Mass Spectra

3-Nitrobenzyl alcohol (M_r 153)

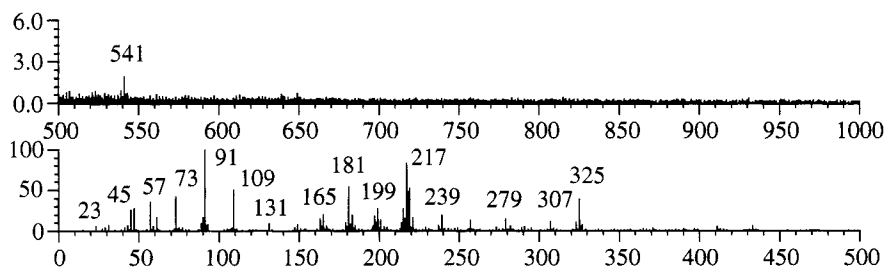


Glycerol (M_r 92)

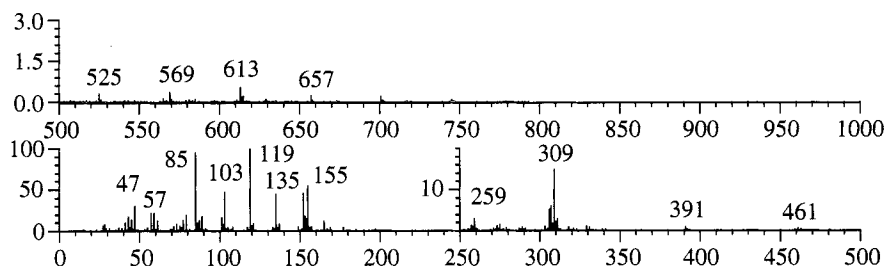


Solvents

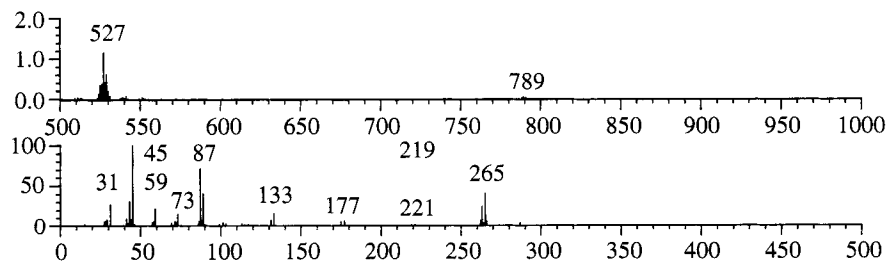
Thioglycerol (M_r 108. Note m/z 23 (Na^+), 131 ($[\text{M}+\text{Na}]^+$), 239 ($[\text{2M}+\text{Na}]^+$). Similarly, small K^+ impurities give signals at m/z 39, 147, 255)



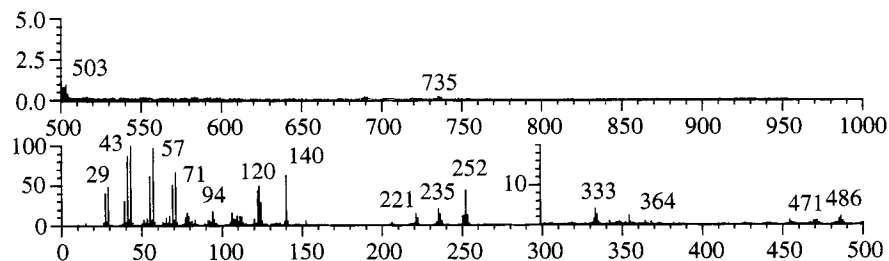
Magic bullet (dithiothreitol/dithioerythritol, $\text{HSCH}_2(\text{CHOH})_2\text{CH}_2\text{SH}$; M_r 154)

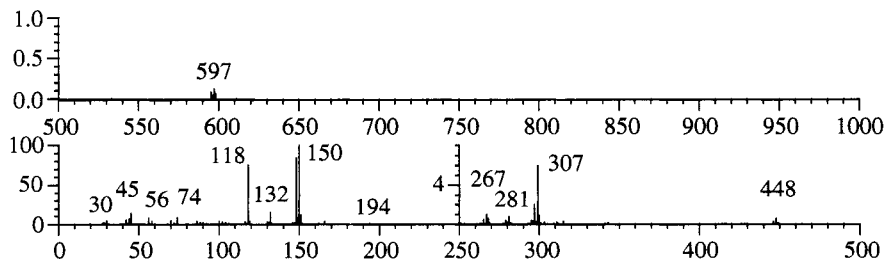
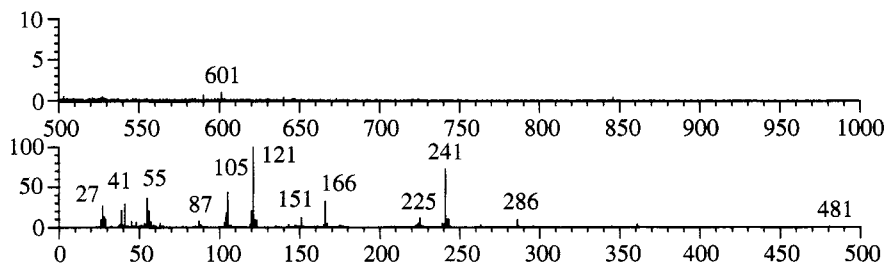
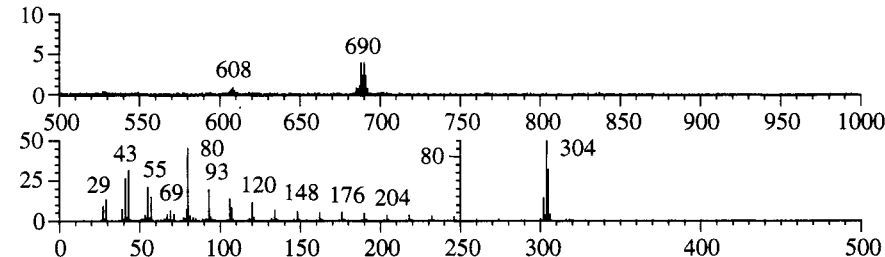


1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6, M_r 264. Also used as an additive; binds metal ions and reduces $[\text{M}+\text{metal ion}]^+$ in favor of $[\text{M}+\text{H}]^+$, which can be important for samples with exchangeable H^+ , such as for peptides [1])

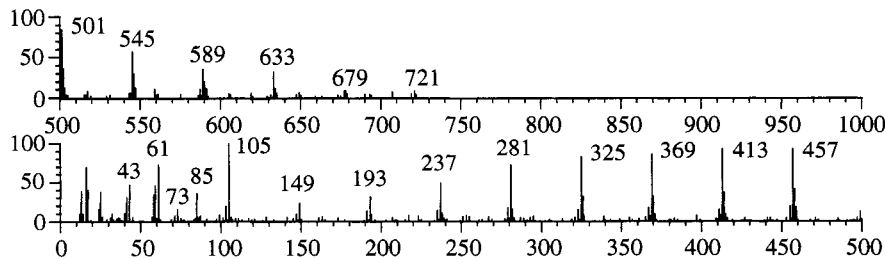


2-Nitrophenyl octyl ether (M_r 251)

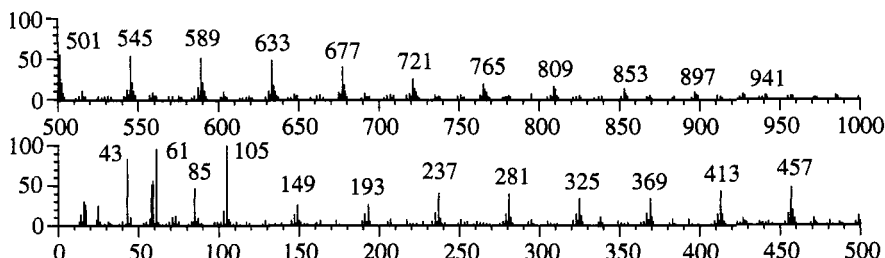


Triethanolamine (M_r 149)Sulfolane (M_r 120) [2]Hexadecylpyridinium bromide (M_r 385; hexadecylpyridinium = 304) in 2-nitrobenzyl alcohol**Calibration Compounds in Negative Ionization FAB Mass Spectra**

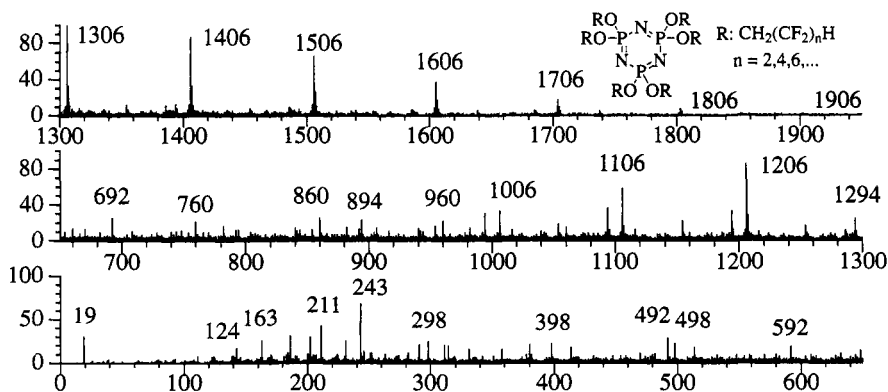
Polyethylene glycol 400 (often used as reference for high resolution MS)



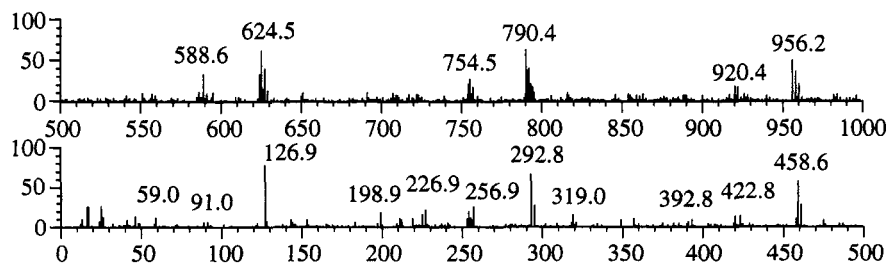
Polyethylene glycol 600 (often used as internal reference for high resolution MS)

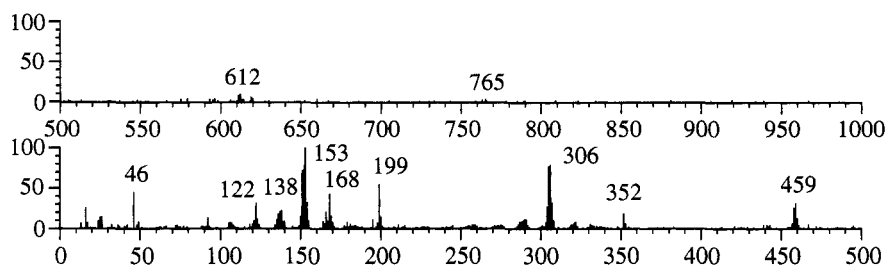
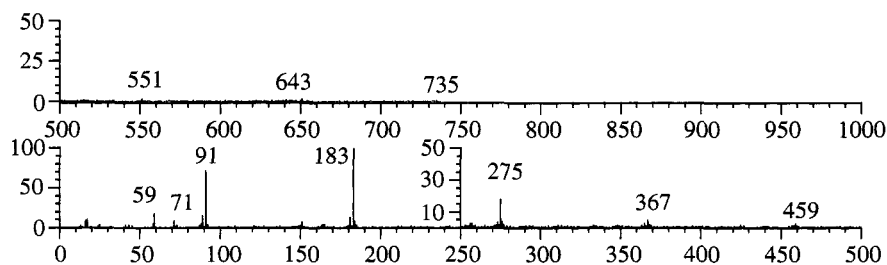
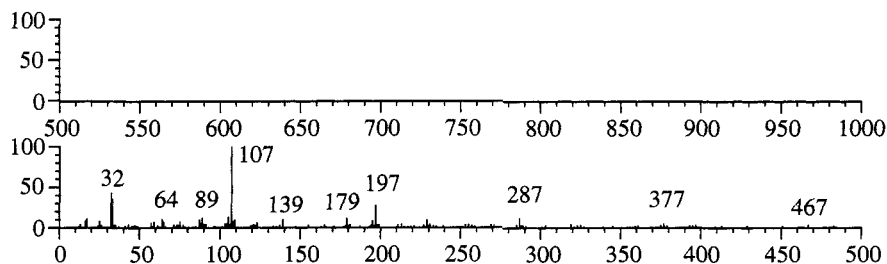
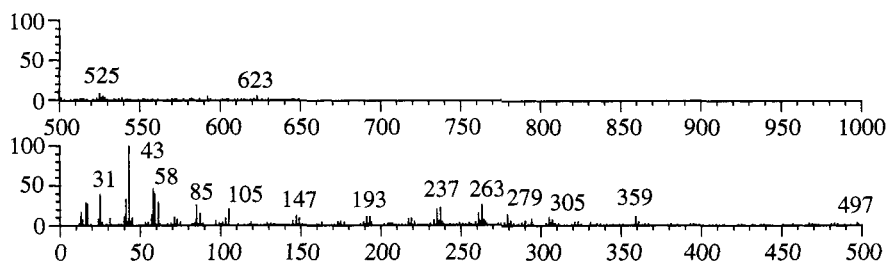


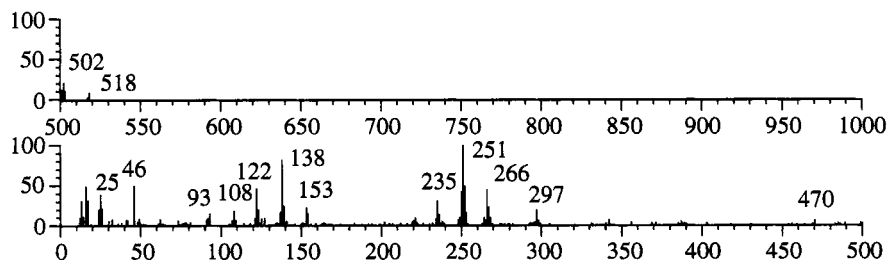
Ultramark 1621 (erroneously also referred to as “perfluoroalkyl phosphazine”)



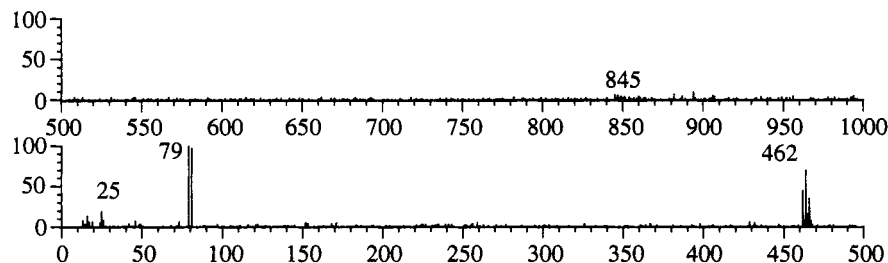
KI (K^+ , 39.0; I^- , 126.9) in glycerol (formation of $[\text{glycerol}_m\text{-H}_n+\text{K}_p+\text{I}_q]^-$)



*Matrix Compounds in Negative Ionization FAB Mass Spectra*3-Nitrobenzyl alcohol (M_r 153)Glycerol (M_r 92)Thioglycerol (M_r 108)1,4,7,10,13,16-Hexaoxacyclooctadecane (18-crown-6, M_r 264)

2-Nitrophenyl octyl ether (M_r 251)

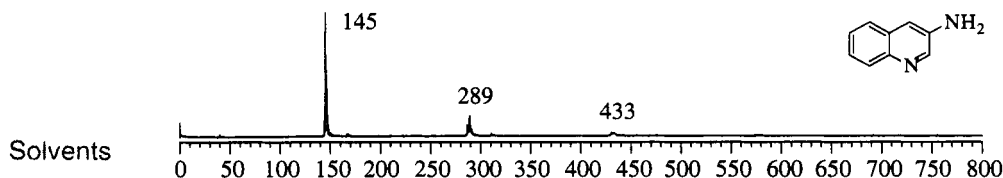
2-Nitrobenzyl alcohol solution of hexadecylpyridinium bromide (M_r 385; hexadecylpyridinium = 304; enhances detectability and reduces metal ion adducts of sample [3].)



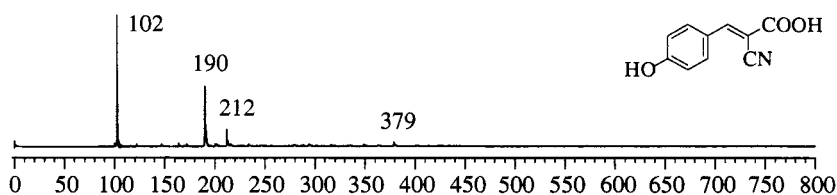
7.13.3

Spectra of Common MALDI MS Matrix Compounds

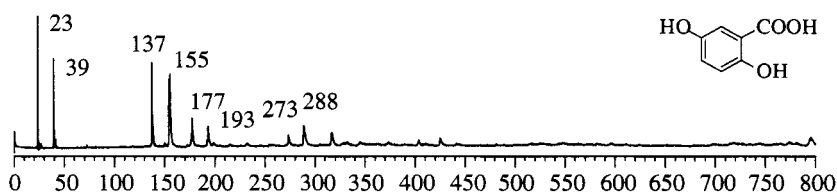
Matrix-assisted laser desorption ionization (MALDI) mass spectra (MS) usually exhibit protonated or deprotonated molecular ions, $[M \pm H]^\pm$, and protonated clusters, $[M_n + X_m \pm H]^\pm$ ($n, m = 0, 1, 2, \dots$), of the sample and matrix molecules, X. If there are even traces of metal salts in the sample, clusters of the type $[M_n + X_m + \text{metal cation}]^+$ occur in positive ionization mass spectra. Sodium (23 u) and potassium (39 u) ion adducts are most commonly encountered. The nature of the clusters is often revealed by the regular intervals at which they occur in the spectra [4].

*Matrix Compounds in Positive Ionization MALDI Mass Spectra*3-Aminoquinoline (M_r 144)

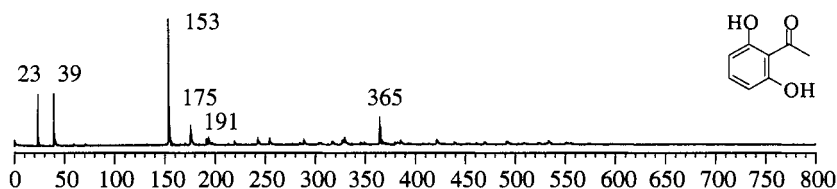
α -Cyano-4-hydroxycinnamic acid (M_r 189; m/z 212, $[M+Na]^+$)



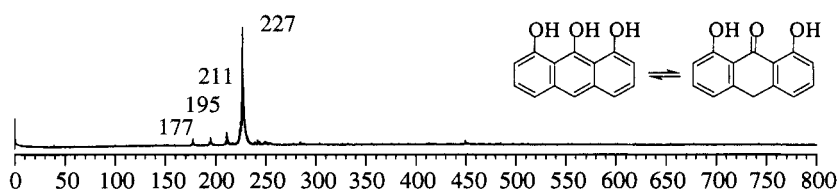
2,5-Dihydroxybenzoic acid (M_r 154; m/z 177, $[M+Na]^+$; m/z 193, $[M+K]^+$)



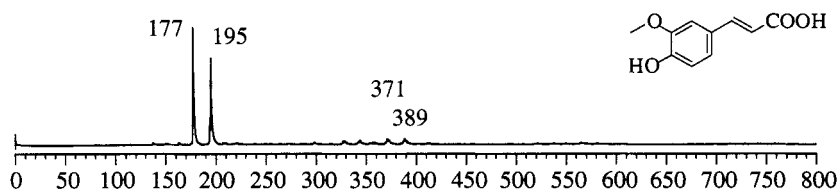
2,6-Dihydroxyacetophenone (M_r 152; m/z 175, $[M+Na]^+$; m/z 191, $[M+K]^+$; m/z 365, $[2M+Na+K-H]^+$?)



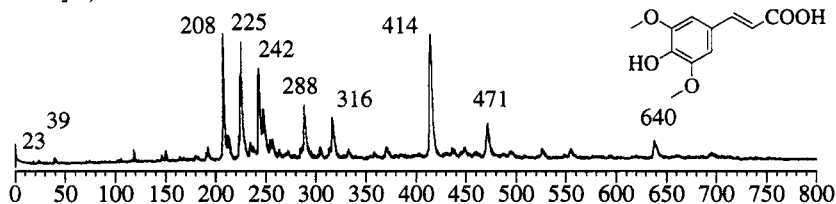
Dithranol (M_r 226)



Ferulic acid (4-hydroxy-3-methoxycinnamic acid; M_r 194)

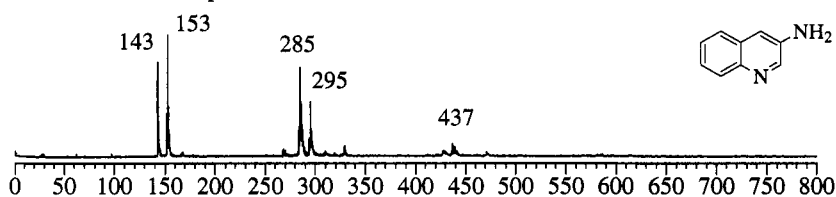


Sinapinic acid (3,5-dimethoxy-4-hydroxycinnamic acid; M_r 224; m/z 471, $[2M+Na]^+$)

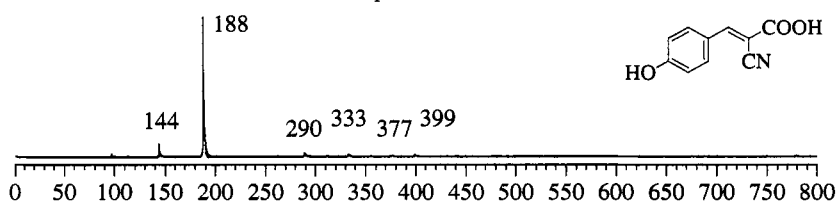


Matrix Compounds in Negative Ionization MALDI Mass Spectra

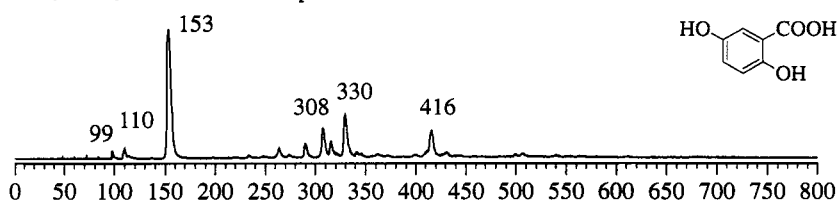
3-Aminoquinoline (M_r 144)



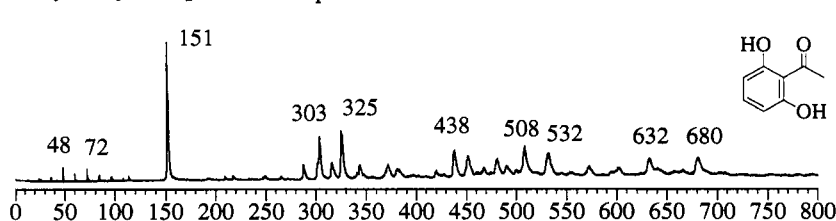
α -Cyano-4-hydroxycinnamic acid (M_r 189; m/z 399, $[2M+Na-2H]^-$)



2,5-Dihydroxybenzoic acid (M_r 154)

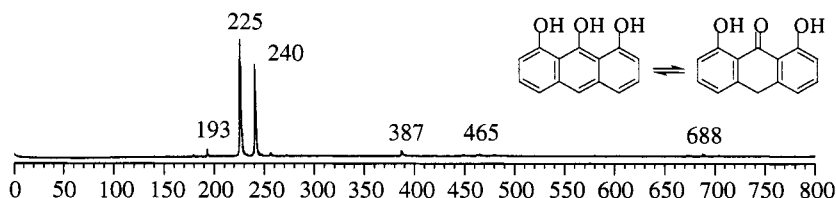


2,6-Dihydroxyacetophenone (M_r 152; m/z 325, $[2M+Na-2H]^-$)

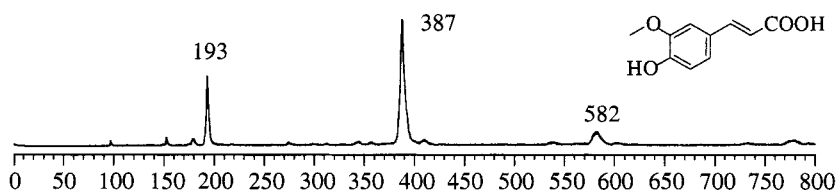


Solvents

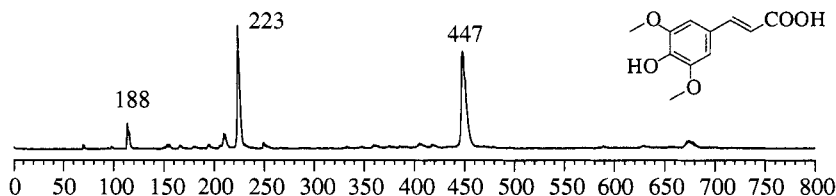
Dithranol (M_r 226)



Ferulic acid (4-hydroxy-3-methoxycinnamic acid; M_r 194)



Sinapinic acid (3,5-dimethoxy-4-hydroxycinnamic acid; M_r 224)



7.13.4 References

- [1] R. Orlando, Analysis of peptides contaminated with alkali-metal salts by fast atom bombardment mass spectrometry using crown ethers, *Anal. Chem.* **1992**, *64*, 332.
- [2] P.K. Singh, L. Field, B. Sweetman, Organic disulfides and related substances, *J. Org. Chem.* **1988**, *53*, 2608.
- [3] Z.-H. Huang, B.-J. Shyong, D.A. Gage, K. R. Noon, J. Allison, *N*-Alkylpyridinium halides: a class of cationic matrix additives for enhancing the sensitivity in negative ion fast-atom bombardment mass spectrometry of polyanionic analytes, *J. Am. Soc. Mass Spectrom.* **1994**, *5*, 928.
- [4] A.E. Ashcroft, *Ionization in Organic Mass Spectrometry*, *RSC Analytical Spectroscopy Monographs*, The Royal Society of Chemistry: Cambridge, 1997.

8 UV/Vis Spectroscopy

8.1

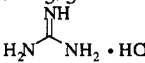

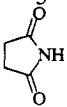
Correlation between Wavelength of Absorbed Radiation and Observed Color

Absorbed light		Observed (transmitted) color
Wavelength [nm]	Corresponding color	
400	violet	yellow-green
425	indigo blue	yellow
450	blue	orange
490	blue-green	red
510	green	purple
530	yellow-green	violet
550	yellow	indigo blue
590	orange	blue
640	red	blue-green
730	purple	green

8.2

UV/Vis Absorption of Simple Chromophores

Chromophore	Compound	Transition	λ_{\max}	ϵ_{\max}	Solvent
C-H	CH ₄	$\sigma \rightarrow \sigma^*$	122	strong	gas
C-C	CH ₃ -CH ₃	$\sigma \rightarrow \sigma^*$	135	strong	gas
C=C	CH ₂ =CH ₂	$\pi \rightarrow \pi^*$	162	15000	heptane
	(CH ₃) ₂ C=C(CH ₃) ₂	$\pi \rightarrow \pi^*$	196	11500	heptane
C=C=C	CH ₂ =C=CH ₂		170	4000	
			227	630	
C \equiv C	CH \equiv CH		173	6000	gas
	<i>n</i> -C ₅ H ₁₁ -C \equiv C-CH ₃		178	10000	hexane
			196	2000	
			222	160	
C-Cl	CH ₃ Cl	$n \rightarrow \sigma^*$	173	200	hexane
C-Br	<i>n</i> -C ₃ H ₇ Br	$n \rightarrow \sigma^*$	208	300	hexane
C-I	CH ₃ I	$n \rightarrow \sigma^*$	259	400	hexane

Chromophore	Compound	Transition	λ_{\max}	ϵ_{\max}	Solvent
C-O	CH ₃ OH	n→σ*	177	200	hexane
	CH ₃ OCH ₃	n→σ*	184	2500	gas
C-N	(C ₂ H ₅) ₂ NH	n→σ*	193	2500	hexane
	(CH ₃) ₃ N	n→σ*	199	4000	hexane
C=N			265	15	water
	(CH ₃) ₂ C=NOH		193	2000	ethanol
	(CH ₃) ₂ C=NONa		265	200	ethanol
	CH ₃ -N=N-CH ₃		340	16	ethanol
N=N	(CH ₃) ₃ C-NO		300	100	ether
N=O			665	20	
	(CH ₃) ₃ C-NO ₂		276	27	ethanol
	<i>n</i> -C ₄ H ₉ -O-NO		218	1050	ethanol
			313-384	20-40	ethanol
	C ₂ H ₅ -O-NO ₂		260	15	ethanol
	CH ₃ CN		<190		
C≡N X=Y=Z	C ₂ H ₅ -N=C=S		250	1200	hexane
	C ₂ H ₅ -N=C=N-C ₂ H ₅		230	4000	
			270	25	
C-S	CH ₃ SH	n→σ*	195	1800	gas
		n→σ*	235	180	
	C ₂ H ₅ -S-C ₂ H ₅	n→σ*	194	4500	gas
		n→σ*	225	1800	
	C ₂ H ₅ -S-S-C ₂ H ₅	n→σ*	194	5500	hexane
C=S		n→σ*	250	380	
	(CH ₃) ₂ C=S		460	weak	
			495	weak	ethanol
C=O	(CH ₃) ₂ C=O	n→σ*	166	16000	gas
		π→π*	189	900	hexane
		n→π*	279	15	hexane
	CH ₃ COOH	n→π*	200	50	gas
	CH ₃ COONa	n→π*	210	150	water
	CH ₃ COOC ₂ H ₅	n→π*	210	50	gas
	CH ₃ CONH ₂	n→π*	220	63	water
			191	15200	CH ₃ CN
C=C=O	(C ₂ H ₅) ₂ C=C=O		227	360	
			375	20	

8.3

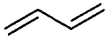
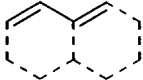


UV/Vis Absorption of Conjugated Alkenes

8.3.1

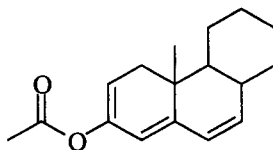
UV Absorption of Dienes and Polyenes

The π - π^* transition of conjugated double bonds is above ≈ 200 nm with typical intensities of the order of $\log \epsilon \approx 4$. Its position can be estimated with the Woodward-Fieser rule. For cross-conjugated systems, the value for the chromophore absorbing at the longest wavelength must be calculated.

Woodward-Fieser rule for estimating the position of the π - π^* transition (λ_{max} in nm)

<i>Parent system</i>		acyclic	217
		heteroannular	214
		homoannular	253
<i>Increments</i>	for each additional conjugated double bond		+30
	for each exocyclic double bond		+5
	for each substituent	C-substituent	+5
		Cl	+5
		Br	+5
		O-alkyl	+6
		OCOCH ₃	0
<i>Solvent correction</i>		N(alkyl) ₂	+60
		S-alkyl	+30
			≈ 0

Example: Estimation of the absorption maximum for



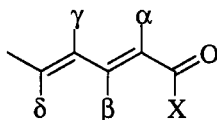
base value (homoannular)	253
1 additional conjugated double bond	30
1 exocyclic double bond	5
3 C-substituents	15
1 OCOCH ₃	0
estimated	303
exp	306

8.3.2

UV Absorption of α,β -Unsaturated Carbonyl Compounds

The $\pi\text{-}\pi^*$ transition of α,β -unsaturated carbonyl compounds is above ≈ 200 nm with typical intensities of the order of $\log \epsilon \approx 4$. Its position can be estimated with the extended Woodward rule. For cross-conjugated systems, the value for the chromophore absorbing at the longest wavelength should be calculated.

Extended Woodward rule for estimating the position of the $\pi\text{-}\pi^*$ transition (λ_{\max} in nm)



Parent system



X: alkyl	215
X: H	207
X: OH	193
X: O-alkyl	193





215



202

Increments for each additional conjugated double bond +30

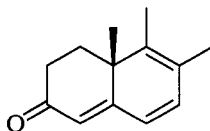
for each exocyclic double bond  +5

for each homoannular diene system  +39

For each substituent on double bond system	Increment			
	α	β	γ	δ and beyond
C-substituent	+10	+12	+18	+18
Cl	+15	+12		
Br	+25	+30		
OH	+35	+30		+50
O-alkyl	+35	+30	+17	+31
O-COCH ₃	+6	+6	+6	+6
S-alkyl		+85		
N(alkyl) ₂		+95		

Solvent corrections	Solvent	Correction term
	water	-8
	hexane	+11
	cyclohexane	+11
	chloroform	+1
	methanol	0
	ethanol	0
	diethyl ether	+7
	dioxane	+5

Example: Estimation of the absorption maximum in ethanol for



base value	215
2 additional conjugated double bonds	60
exocyclic double bond	5
homoannular diene system	39
1 β -C-substituent	12
3 additional C-substituents	54
solvent correction	0
estimated	385
exp	388

8.4

UV/Vis Absorption of Aromatic Compounds

8.4.1

UV Absorption of Monosubstituted Benzenes

Typical Ranges for Monosubstituted Benzenes

Transition	λ_{\max}	ϵ
$\pi \rightarrow \pi^*$ (allowed)	180–230	2000–10000
$\pi \rightarrow \pi^*$ (forbidden)	250–290	100–2000
$\pi \rightarrow \pi^*$ (substituent delocalized by aryl; K Band)	220–250	10000–30000
$n \rightarrow \pi^*$ (substituent with lone pair; R band)	275–350	10–100

Specific Examples of Monosubstituted Benzenes

Substituent R (solvent)	$\pi \rightarrow \pi^*$ (allowed)		$\pi \rightarrow \pi^*$ (forbidden)		$\pi \rightarrow \pi^*$ (K band)		$n \rightarrow \pi^*$ (R band)	
	λ_{\max}	ϵ	λ_{\max}	ϵ	λ_{\max}	ϵ	λ_{\max}	ϵ
–H (cyclohexane)	198	8000	255	230				
–CH ₃ (hexane)	208	7900	262	230				
–CH=CH ₂ (ethanol)			282	450	244	12000		
–C≡CH (hexane)			278	650	236	12500		
–Cl (ethanol)	210	7500	257	170				
–OH (water)	211	6200	270	1450				
–O [–] (water)	235	9400	287	2600				
–NH ₂ (water)	230	8600	280	1430				
–NH ₃ ⁺ (water)	203	7500	254	160				
–NO ₂ (hexane)	208	9800	270	800	251	9000	322	150
	213	8100						
–CN (water)			271	1000	224	13000		
–CHO (hexane)			280	1400	242	14000	≈330	≈60
–COCH ₃ (ethanol)			278	1100	243	13000	319	50
–COOH (water)	202	8000	270	800	230	10000		

8.4.2

UV Absorption of Substituted Benzenes

Estimation of the position of the allowed π - π^ transition in multiply substituted benzenes (λ_{max} in nm, $\log \epsilon$: ≈ 4)*

Base value: 203.5

Substituent	Increment [nm]
-CH ₃	3.0
-Cl	6.0
-Br	6.5
-OH	7.0
-O ⁻	31.5
-OCH ₃	13.5
-NH ₂	26.5
-NHCOCH ₃	38.5
-NO ₂	65.0
-CN	20.5
-CHO	46.0
-COCH ₃	42.0
-COOH	25.5

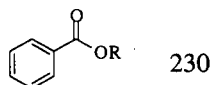
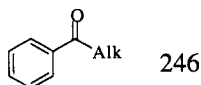
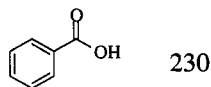
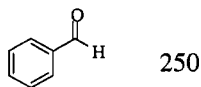
8.4.3

UV Absorption of Aromatic Carbonyl Compounds

Scott rules for estimating the position of the K band

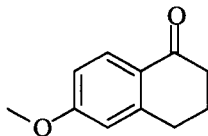
(solvent: ethanol; λ_{\max} in nm, ϵ : 10000–30000)

Parent system:



Increments	Substituent	<i>ortho</i>	<i>meta</i>	<i>para</i>
	–alkyl	3	3	10
	–cycloalkyl	3	3	10
	–Cl	0	0	10
	–Br	2	2	15
	–OH	7	7	25
	–O–alkyl	7	7	25
	–O [–]	11	20	78
	–NH ₂	13	13	58
	–N(CH ₃) ₂	20	20	85
	–NHCOCH ₃	20	20	45

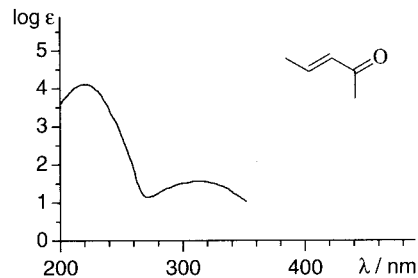
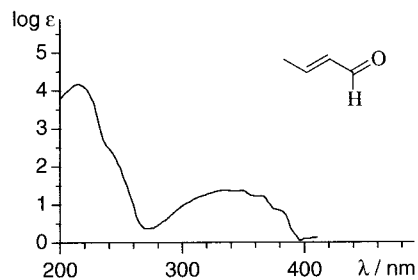
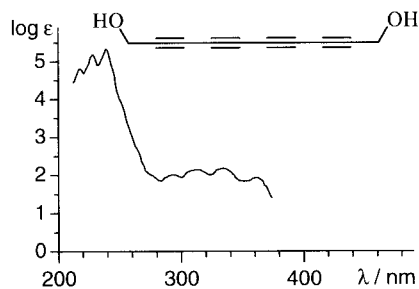
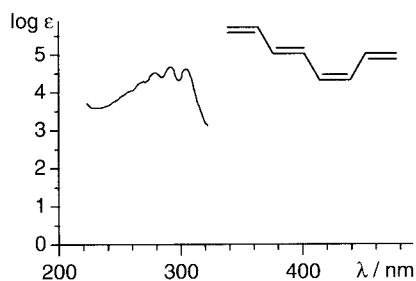
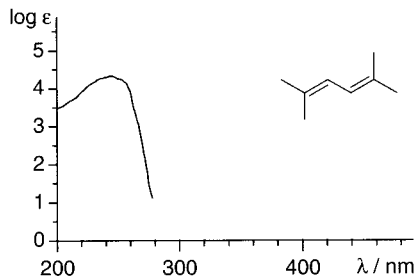
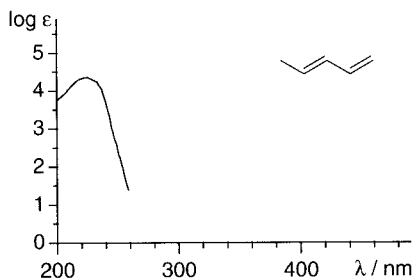
Example: Estimation of the absorption maximum (K band) for

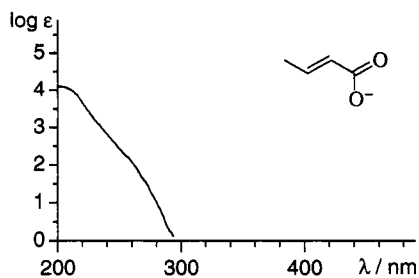
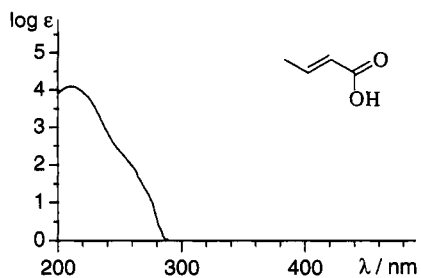


base value	246
<i>ortho</i> -cycloalkyl	3
<i>para</i> -O-alkyl	25
estimated	274
exp	276

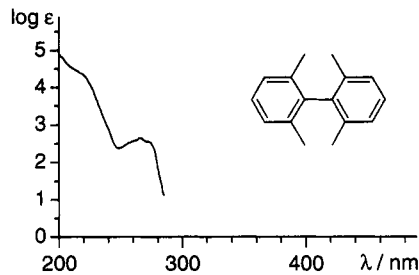
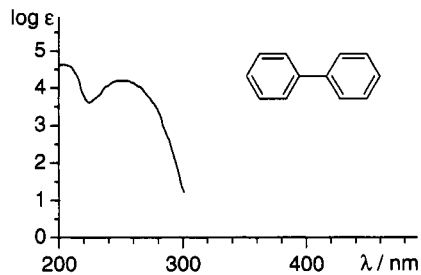
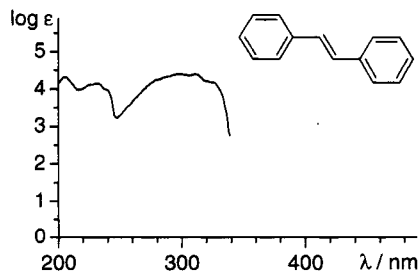
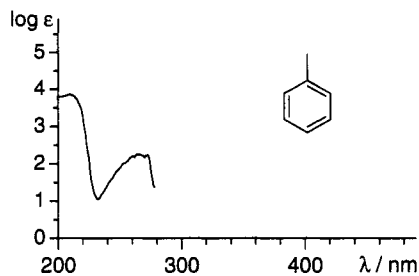
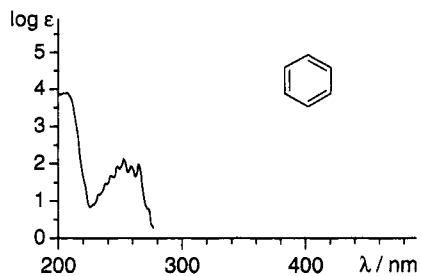
8.5 UV/Vis Reference Spectra

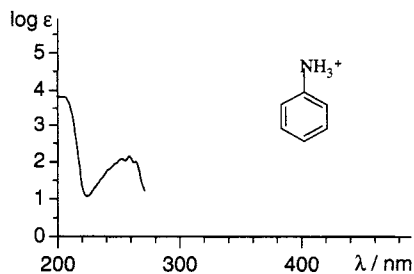
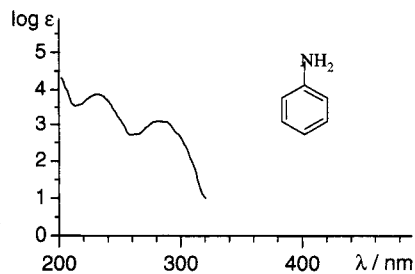
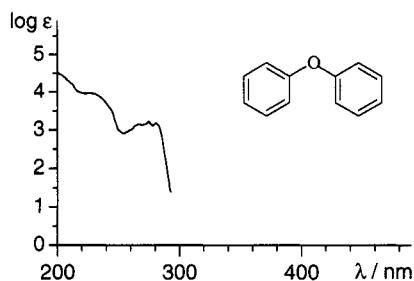
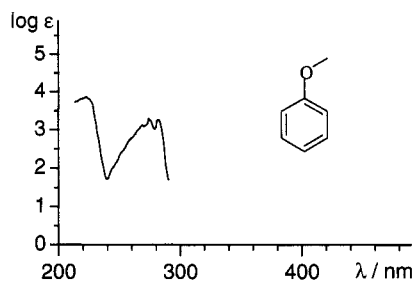
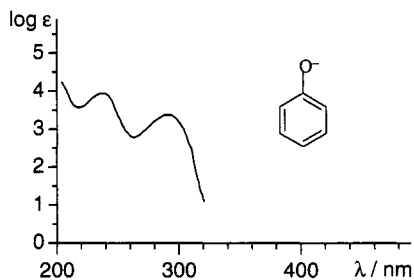
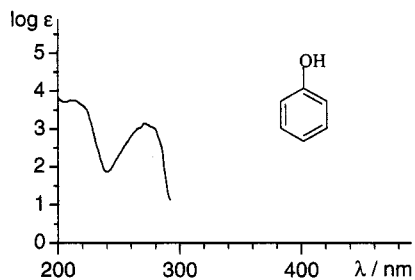
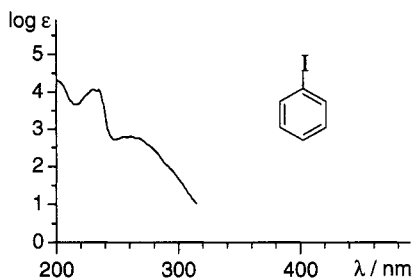
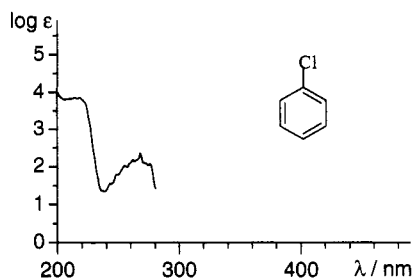
8.5.1 UV/Vis Spectra of Alkenes and Alkynes

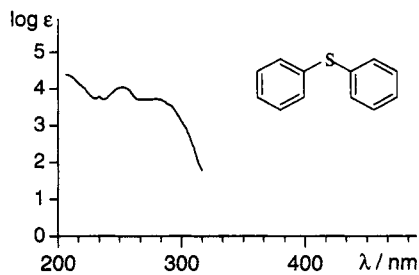
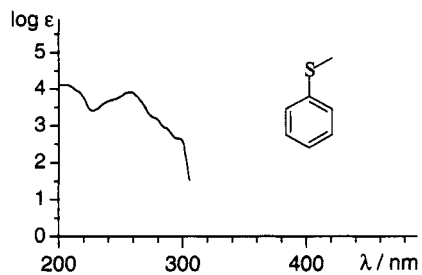
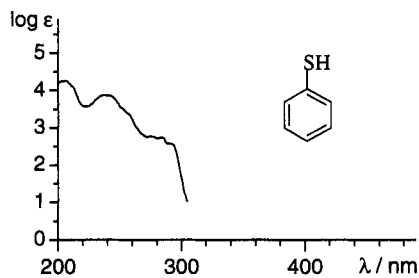
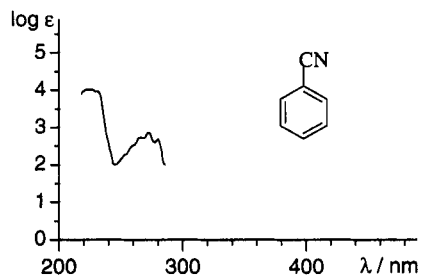
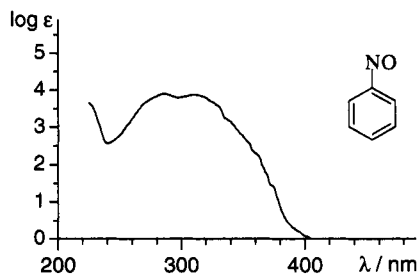
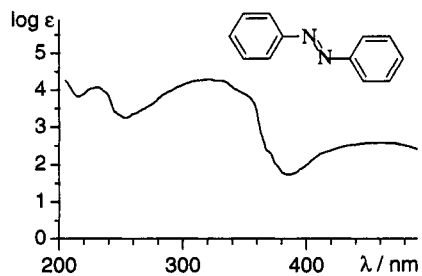
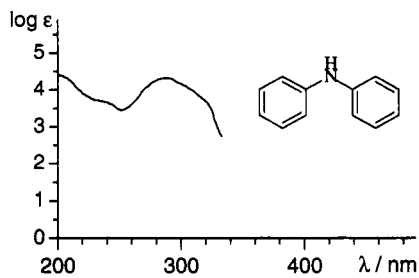
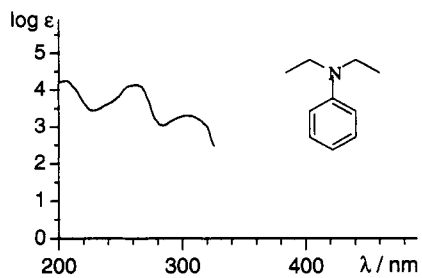


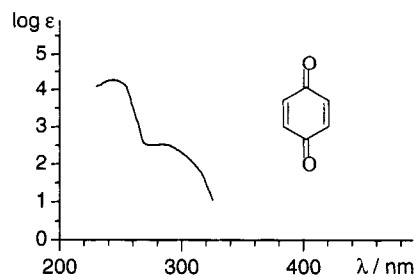
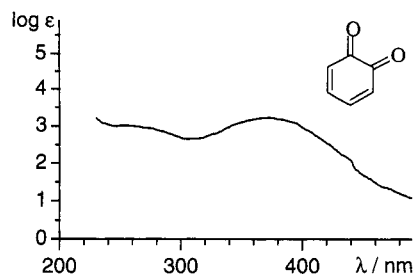
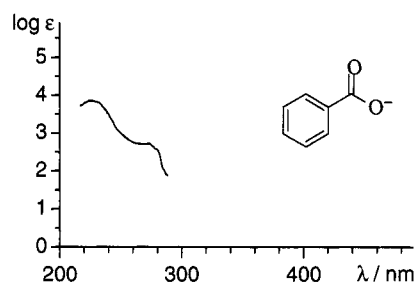
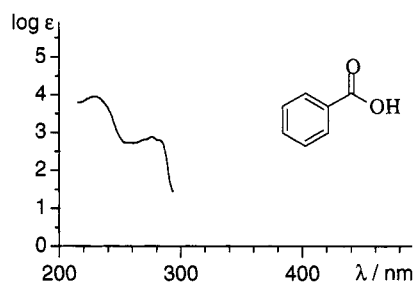
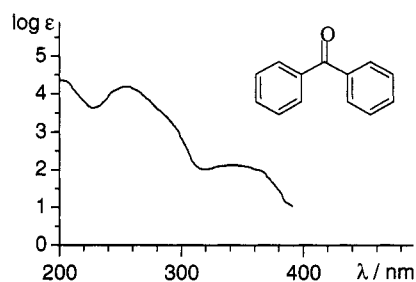
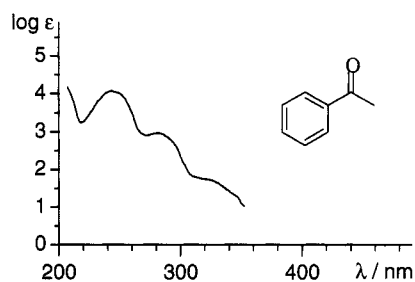
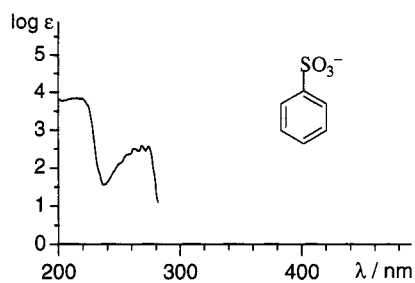


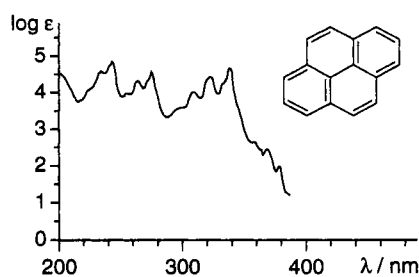
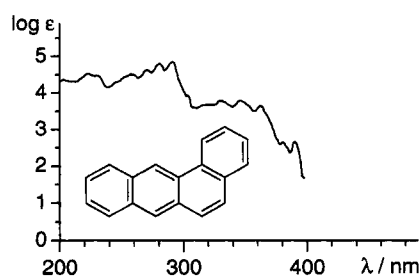
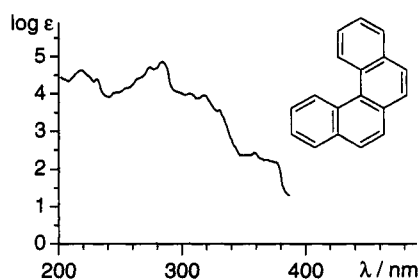
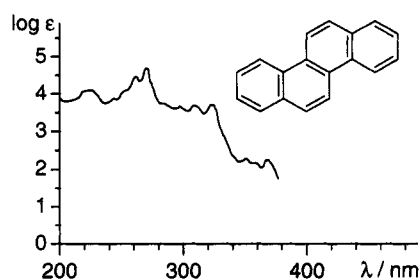
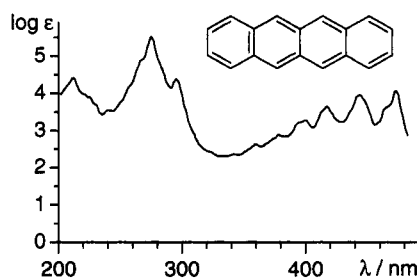
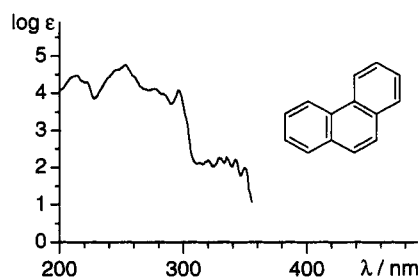
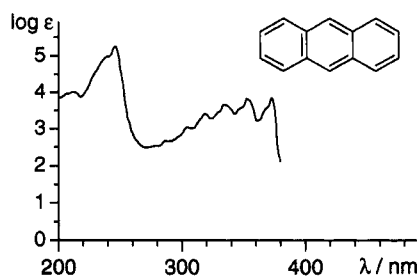
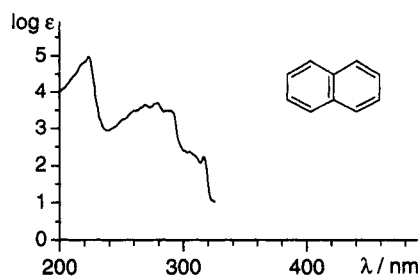
8.5.2 UV/Vis Spectra of Aromatic Compounds

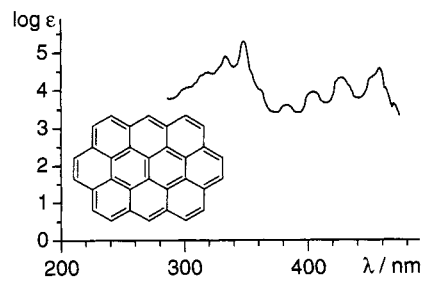
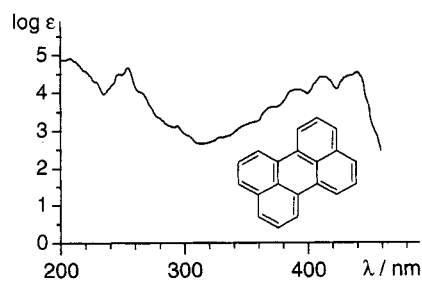
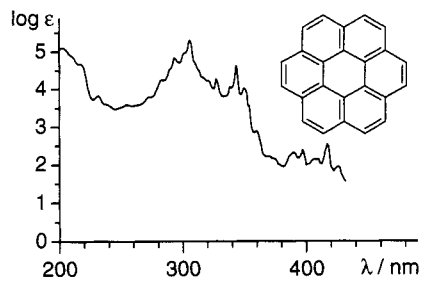
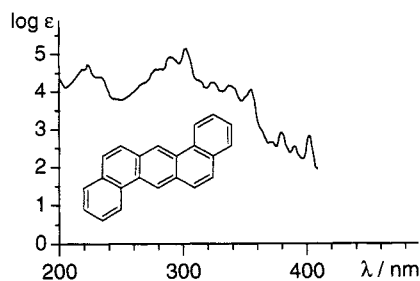
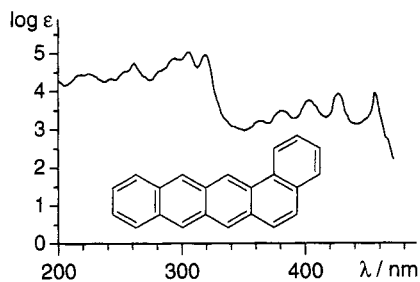
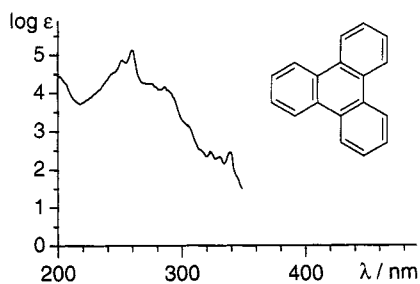




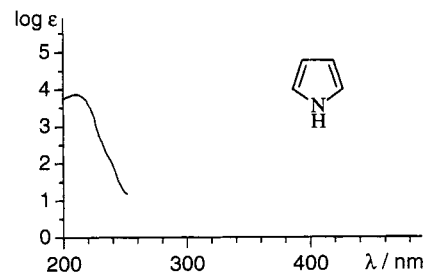
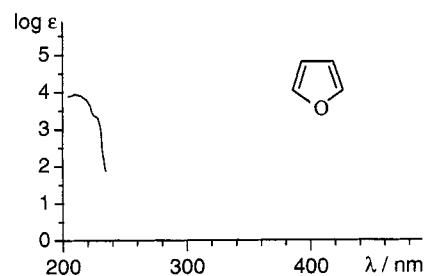


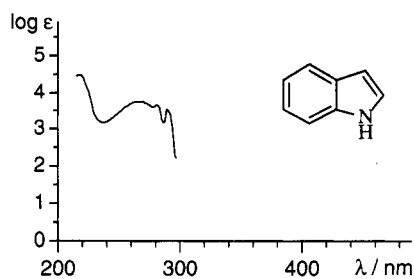
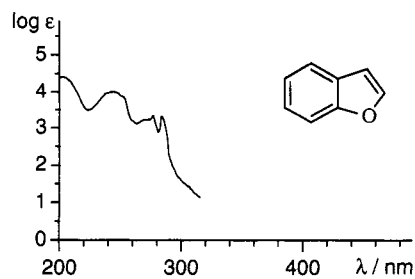
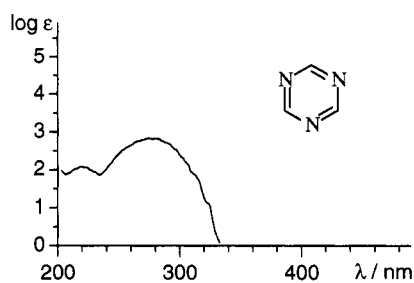
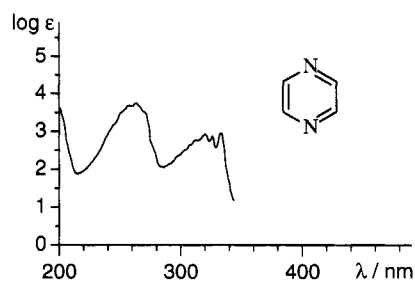
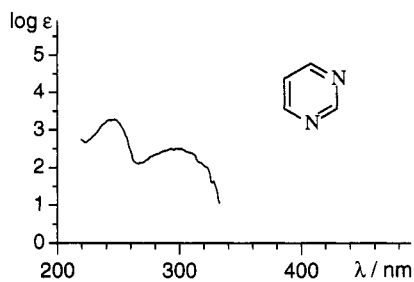
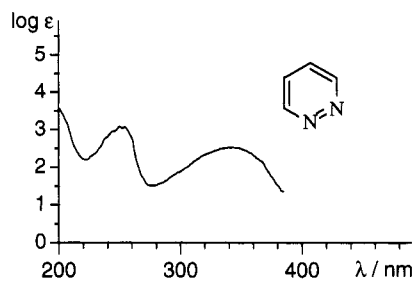
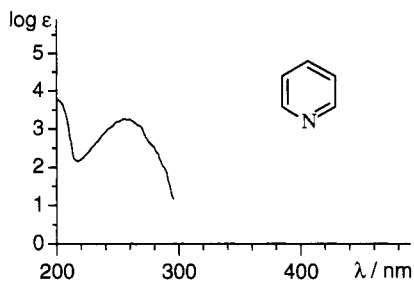
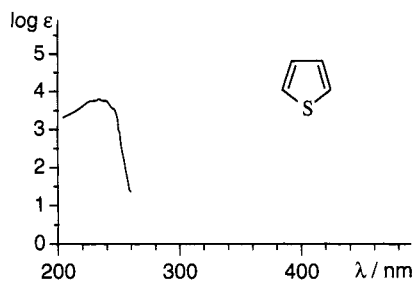


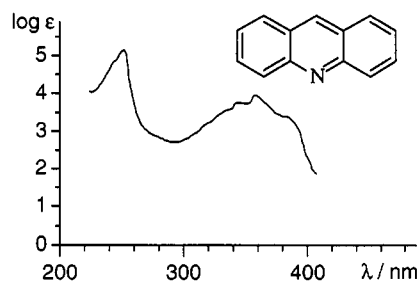
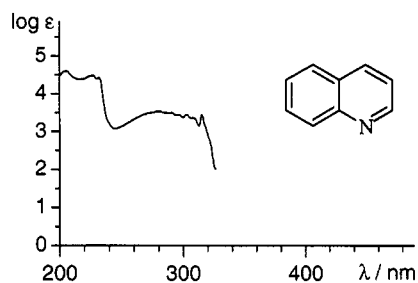
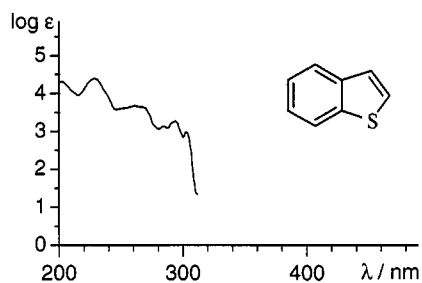




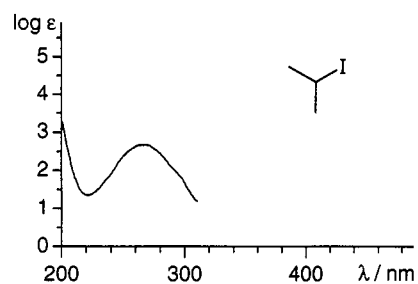
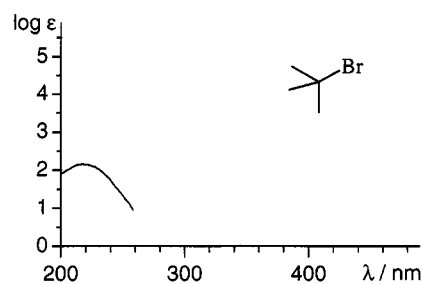
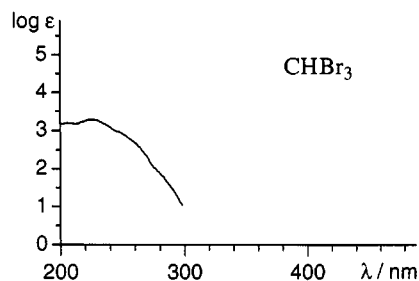
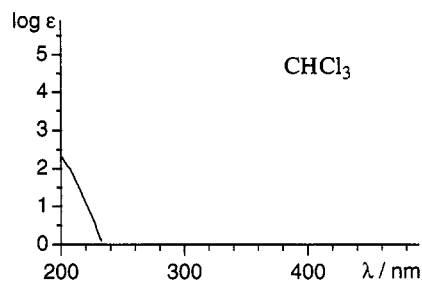
8.5.3 UV/Vis Spectra of Heteroaromatic Compounds

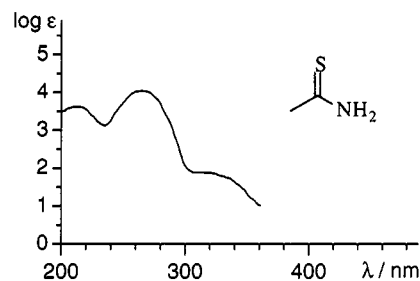
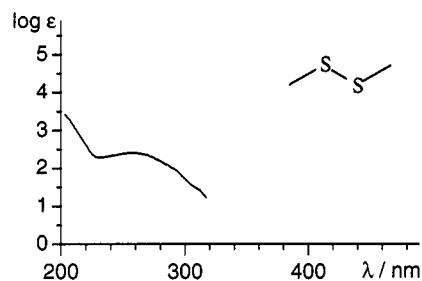
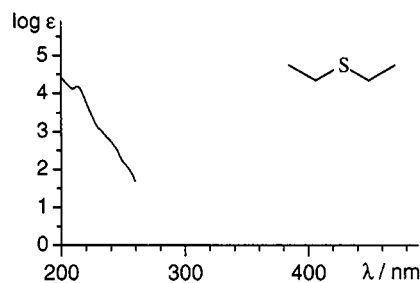
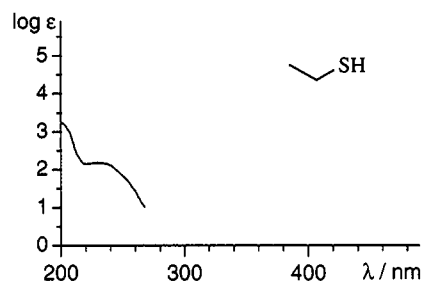
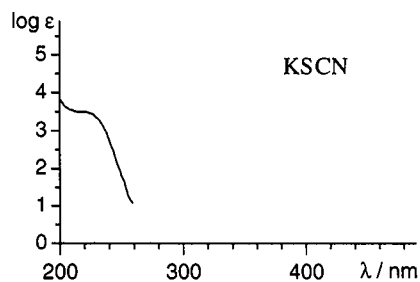
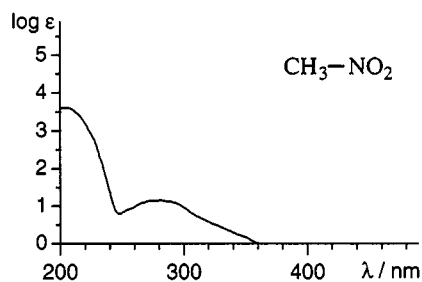
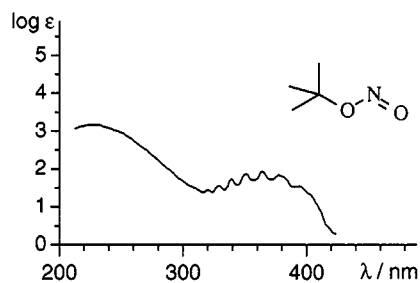
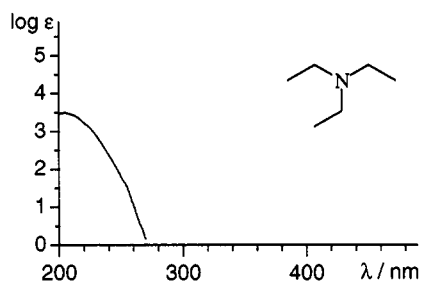


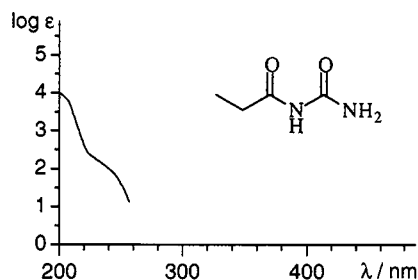
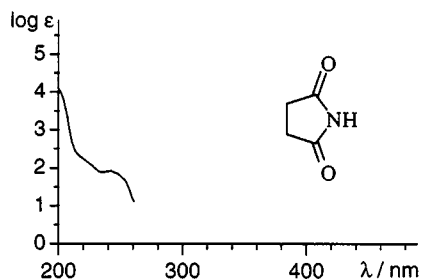
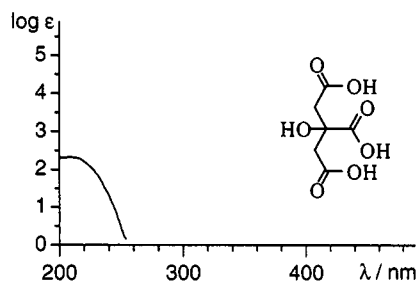
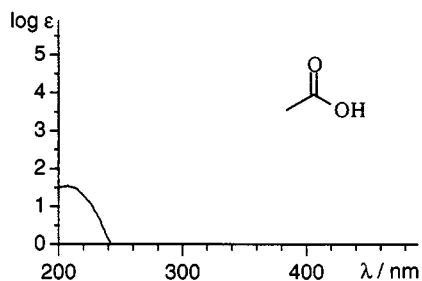




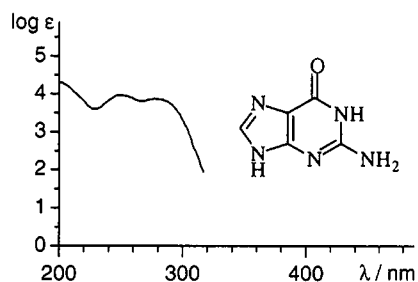
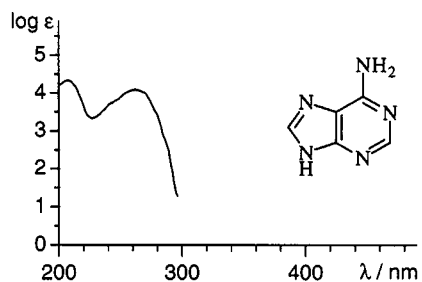
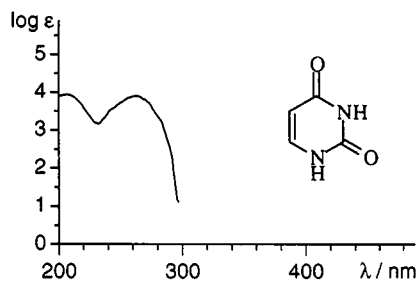
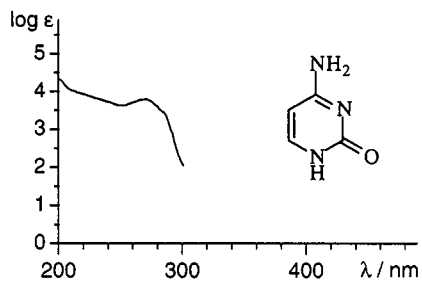
8.5.4 UV/Vis Spectra of Miscellaneous Compounds







8.5.5 UV/Vis Spectra of Nucleotides



8.6

UV/Vis Absorption of Common Solvents

The end absorption, λ_{end} , of several common solvents is given here as the wavelength at which the solvents absorb 80% of the irradiated light (λ_{end} in nm; cell length, 1 cm; reference, water).

Solvent	λ_{end}	Solvent	λ_{end}
acetone	335	ethyl acetate	205
acetonitrile	190	heptane	195
benzene	285	hexane	195
carbon disulfide	380	methanol	205
carbon tetrachloride	265	pentane	200
chloroform	245	2-propanol	205
cyclohexane	210	pyridine	305
dichloromethane	230	tetrahydrofuran	230
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Acenaphthylene	C96	H181			
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Acetaldoxime	H211	I274			
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	U403				
– esters	C138				
– anhydride	C142	H226	I299		
Acetoisonitrile	C126				
Acetone	C81	C134	C160	H219	
	H243	M371	U405		
– dimethylhydrazone	C125				
Acetone- <i>d</i> ₆	C157	H240			
Acetonitrile	C126	C160	H212	H243	
	M371	U405			
Acetonitrile- <i>d</i> ₃	C157	H240			

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Acetyl bromide	C142	H226		
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Acetyl chloride	C142	H226		
– iodide	C142			
<i>N</i> -Acetyl pyrrolidine	H225			
<i>N</i> -Acetyl- γ -valerolactam	H227			
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Acetylenic ethers	M334			
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– chlorides	4	6	32	40
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– fluorides	I300			
– halides	C142	H226	I300	
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	14	15	32	33
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– aliphatic	M360			
– aromatic	M361			

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– α,β -unsaturated	U388			
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Acrylaldehyde	C133	H218		
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– branched	M315			
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